Synthesis and characterization of $AgBr/SiO_2$ core/shell nanoparticles

Thesis submitted

by

MINAKETAN RAY
(608CH601)

In partial fulfillment for the award of the Degree of

Master of Technology (Research)

In

Chemical Engineering

Under the guidance of

Dr. Santanu Paria

DEPARTMENT OF CHEMICAL ENGINEERING
NATIONAL INSTITUTE OF TECHNOLOGY,
ROURKELA-769008, ODISHA, INDIA.
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CERTIFICATE

This is to certify that the thesis entitled **"Synthesis and characterization of AgBr/SiO_2 core/shell nanoparticles."** submitted by "Mr. Minaketan Ray" in partial fulfillments for the requirements for the award of Master of Technology by Research Degree in Chemical Engineering to the National Institute of Technology, Rourkela (Deemed University). He has been authentic work carried out under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any Degree or Diploma.

Date:

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ACKNOWLEDGEMENTS

First, I would like to thank my research supervisors, Dr. S. Paria. I could not have imagined having a better advisor and mentor for my M.Tech (R), and without your excellent guidance and continuous support, knowledge and perceptiveness I would never have finished. I learnt so much from you that I will always be indebted for all the research skills you have cultivated in me.

My special thanks to Prof. R. K. Singh, HOD, Department of Chemical Engineering, for agreeing to become chair of my committee in a very short notice and providing official support. I would like to thanks entire faculty of the Chemical Engineering Department for their support.

I am also thankful to the Metallurgical and Materials Engineering for allowing me to use FTIR and SEM for sample analysis and also Ceramic Engineering Department for to conduct X-ray analysis during my project work.

There are many people to thank for their support and encouragement, without which this milestone would be an unattainable dream. I want to thank my research group including Mr. Nihar rajan Biswal, Mr. Rajib Ghosh Chaudhuri, Mr. K. Jagajjanani Rao, Mr. Navin N, Jason, for their valuable suggestion and help during the course work and research work and my friends in the department who have made the last few years an exciting and memorable experience.

I express my deep thanks to my parents, my brother and my sister for all their love and support. Their encouragement and guidance have provided throughout my academic career and for standing beside me whenever I needed a backing.

Place: Rourkela

Date: Mr. Minaketan Ray

Contents

ABSTRACT

In the recent years there is tremendous demand of smaller devices over the bigger one because of its efficiency and portability. The nanoparticles are the building blocks to make the very small devices like small robot, micro-motor, small chips, microprocessor, sensor or carrier for drugs or storage for fuel cell etc. So small is not only beautiful but also powerful.

To improve the property of nanoparticle, composite or core/shell nanoparticles are synthesized. The core-shell nanoparticles are used in the field of biotechnology for drugs carrier, in electronic as semiconductor materials, in fuel-cell and also in chemical reaction. The easy and generalization of methods is required to prepare the core-shell nanoparticles. In this study we prepared core-shell nanoparticles, where AgBr is core and silica as a shell material. For preparation of core-shell nanoparticles, precipitation and the modified Stöber method were adopted. The surfactant is used to modify the surface of core particle so that core-shell nanoparticle will form. Before going to core-shell particles, the individual particles of AgBr and SiO_2 were studied. Spherical AgBr nanoparticles were prepared in aqueous media in the absence and presence of surfactant. Smaller particles were obtained in pure aqueous media by increasing the reactant concentration. The coarsening rate constant for the particle formation was found to increase linearly with increasing reactant concentration. The presence of nonionic surfactant generated smaller particles than were obtained in pure aqueous media. The coarsening rate constant in the presence of TX-100 was always lower than that in the presence of pure aqueous media. In pure aqueous media, the temperature effect caused an increase in particle size as the temperature was increased from 20 to 30 °C, after which the change was not significant. In contrast, in the presence of TX-100, the change was not significant in the 20 - 30 °C temperature ranges, but a further increase to 40 °C resulted in a significant change in size. Silica is coated on

AgBr nanoparticles by modified Stöber methods. The lowest particles size of the $AgBr/SiO_2$ core-shell was 90±8 nm. The core-shell particle sizes varied from 95 nm to 430 nm. It is found that the bigger particle size found on higher concentration of TEOS. The CTAB surfactant assist-AgBr nanoparticles were isolated in silica shell, indicates CTAB concentration (0.1 mM) were optimal for the formation of monolayered structures on AgBr surfaces. The shell thickness was very thin 5 nm. The $AgBr/SiO_2$ core/shell nanoparticles have been prepared within 100 nm by modified Stöber methods. The spherical composite materials are formed. The shell thickness can be controlled on varying the concentration of precursor's solution. Silica can be coated on other material by modifying the surface of the core shell materials.

Keywords: Core-shell nanoparticles, $AgBr/SiO_2$, Growth kinetics, Silver Bromide nanoparticles, Silica nanoparticles, surfactant media, modified stöber method.

LIST OF FIGURE

LIST OF TABLES

ACRONYMS

CMC	Critical micelle concentration
CTAB	Cetyl trimethyl ammonium bromide
DLS	Dynamic light scattering
FTIR	Foriour transformation infra red
NP	Nano particle
SDBS	Sodium dodecyl benzene sulphonate
SDS	Sodium dodecyl sulphate
SEM	Scanning electron microscope
TEM	Transmission electron microscope
TX-100	Triton X-100
Uv	Ultra violet
XRD	X-ray diffraction

Chapter-1

General Introduction

1.1 Introduction

Nanotechnology is considered as the technology of the 21^{st} century, following the microtechnology development and now, even if we do not realize it yet, these materials are already taken a remarkable part in our everyday life. What qualifies as "nanotechnology" today is basic research and development that is happening in laboratories all over the world. "Nanotechnology" products that are on the market today are gradually improved products (using *evolutionary* nanotechnology) where some form of nanotechnology enabled material (such as carbon nanotubes, nanocomposite structures or nanoparticles of a particular substance) or nanotechnology process (e.g. nanopatterning or quantum dots for medical imaging) is used in the manufacturing process. In their ongoing quest to improve existing products by creating smaller components and better performance materials, all at a lower cost, the number of companies that will manufacture "nanoproducts" will grow very fast and soon make up the majority of all companies across many industries. Evolutionary nanotechnology should therefore be viewed as a process that gradually will affect most companies and industries.

1.2 Definition of Nanotechnology

Nano is used as prefix for a unit of Time or length, denoting a factor of 10^{-9}.The "nano" originates from the Greek word nanos, meaning dwarf, something small. The nanomaterials can be defined as when at least one dimension of the material is below 100 nm among the three dimensions, called nanomaterials. If three dimensions are less than 100 nm, it's called as nanoparticles.

Nanoscience can be defined as the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger

scale; and nanotechnologies as the design, characterisation, production and application of structures, devices and systems by controlling shape and size at the nanometer scale. In some senses, nanoscience and nanotechnologies are not new. Chemists have been making polymers, which are large molecules made up of nanoscale subunits, for many decades. However, advances in the tools that now allow atoms and molecules to be examined and probed with great precision have enabled the expansion and development of nanoscience and nanotechnologies.

The most important requirement for the nanotechnology definition is that the nano-structure has special properties that are exclusively due to its nanoscale proportions. In nano scale, some of the particle properties differ from bulk property. The nanoparticles show peculiar property depending on its size and shape. There are many interesting areas in nanotechnology. One of the most important aspects of this field is the preparation and development of nanomaterials, such as nanoparticles. There have been a variety of techniques for preparing different types of nanoparticles.

1.3 Type of Nanoparticles

There are different type of nanoparticles are designed on focusing to their potential application in different field of technology. On the basis of shape, it can be categorized into cubic shape, spherical shape, cylindrical or hexagonal etc. similarly if we will focus on size it may be different type like 1-Dimensional nanoparticles or crystals, 2D or 3D etc. But broadly it can be divided into two types-

Nanoparticles

Hollow nanoparticle

Nanoparticles can be defined as materials and systems whose structures and components exhibit novel and significantly improved physical, chemical and biological properties, phenomena and processes due to their nanoscale size (1-100 nm).

Recently hollow nanoparticles have attracted considerable research attention due to their large variety application in chemistry, biotechnology, and material science. The name hollow itself indicates that it has two surfaces inner and outer. The inner side of the particles is empty. That's why it can act as carrier for particular purpose.

Here we have been focused on core-shell nanoparticles. The hollow nanoparticles can synthesize by removing the core particles. The synthesis techniques for core-shell and hollow nanoparticles are given below.

1.4 Synthesis Technique

There are various chemical and physical technique have been developed to synthesis of the nanomaterials. Broadly it can be divided into two main categories as top-down and Bottom-up approach.

1.4.1 Top-down approach

Nanoparticles are created by these methods from breaking up the bulk materials. Attrition, milling is a typical top-down approach. The bigger particles or structures are broken into very small pieces to reach into nano scale. So the biggest problem is the imperfection of the surface structure. It is the well known conventional methods to prepare nanoparticles. The top-down technique such as lithography can cause significant crystal graphic damage to processed patterns and additional defects may introduce during etching (Burton et al., 1949). Lithography can be understood through the concepts of writing and replication. Writing involves designing a pattern

on a negative and replication involves transferring the pattern on the negative to a functional material. There are several types of lithography. Photolithography, which uses different kinds of electromagnetic radiation, is currently used to manufacture computer chips and other microelectronic devices. Photolithography, as currently used, is not an effective tool for fabricating structures with features below 100 nanometers. E-beam lithography, a technique that employs beams of electrons to write, can produce some nanostructures with high resolution. Soft lithographic techniques, such as printing, molding, and embossing, involve the physical or chemical deformation of the functional material to yield the desired structure. While soft lithography can be used to construct less planar nanostructures, it may be less precise than other techniques. This approach most likely introduces internal stress, in addition to surface defects and contaminations.

1.4.2 Bottom-up approach

In general, bottom-up is widely used and less energy intensive. Bottom-up approach is nothing new in materials synthesis. Typical materials are building up atom by atom on a large scale with control of size and shape of the materials. This approach is just opposite of Top-down approach. The materials are synthesized, taken care of it from atomic levels. So the nanomaterials are formed from the bottom levels atom by atom, molecule by molecule or cluster by cluster. In organic chemistry or polymer science, we know polymers are synthesized by connecting individual monomers together. In crystal growth, growth species, such as atoms, ions and molecules, after impinging onto the growth surface, assemble into crystal structure one after another.

It plays an important role on fabrication and processing of nanostructure and nanomaterials. Bottom-up approach also promises a better chance to obtain nanostructures with less defects, more homogeneous chemical composition, and better short and long range ordering. This is because the bottom-up approach is driven mainly by the reduction of Gibbs free energy, so that nanostructures and nanomaterials such produced are in a state closer to a thermodynamic equilibrium state.

Several methods have been developed to synthesis nanoparticle in bottom-up approach. The method used to synthesis can be categories into liquid phase synthesis or vapor phase synthesis. The most common method is liquid phase synthesis. There are various methods belong to liquid phase synthesis like sol-gel method, simple reaction methods (aqueous solution), reverse emulsion or microemulsion methods, spry precipitation methods. But in vapor phase synthesis, the chemical vapor deposition is the most common methods.

1.4.3 Simple reaction methods

The precipitation reaction is the most common in wet chemical methods to produce particles and powders. The majority of products in the chemical industry undergo crystallization/precipitation at some stage of their manufacture. Crystallization occurs when a solution is cooled to such an extent that it becomes supersaturated leading to nucleation and crystal formation. When an insoluble product is formed because of a chemical reaction between reactant called precipitation reaction. In both cases the product usually requires filtration, washing and drying and sometimes calcination steps. The most effort in using these two techniques for nanoparticle production has come from the pharmaceutical and catalyst production sectors by reason that increasing surface area will enhance chemical reactivity and dissolution. The products for application in both areas

usually demand high purity with well-defined specifications and to meet these requirements well-controlled processes have been developed. The greatest challenge in using these nanoparticle production approaches for pharmaceutical and catalytic application is to control the size, shape and stability of the product. Many nanoparticles have been prepared by these methods. The particles are formed by these methods the diameter ranges from 20 nm to some micrometer. The small nanoparticles are formed by use of some mechanical force or chemical methods or surface active agent to restrict the growth of the nanoparticles.

1.4.4 Spry Precipitation methods

A spray precipitation method is disclosed that is enabling to synthesize high yield of nano and micro hollow spheres in a liquid / liquid system. (Linyong et al., 2006; Chung et al., 2004) Microfabrication of Al_2O_3, TiO_2 and ZrO_2 hollow particles were carried out by spray precipitation. In this spray precipitation process one liquid solution is sprayed over another liquid surface. Solid precipitation formed on the contact angle of two liquid. A spray technique is to atomize the precursor solution into nano or micro meter scale droplets. The droplets are put into a precipitation agent. The precipitation agents are including dehydration or neutralization agents. The rapid dehydration or hydrolysis occurs at the interface of two liquid, which leads to formation of rigid shell. This method allows producing nano and micro meter sized hollow sphere particles. The diameters of the hollow particles are prepared varied from 20-70 μm. There are various parameter are responsible for the variation of the diameter.

1.4.5 Sol-Gel reaction

The terms sol-gel processing involves the transition from a sol (very finely divided solid particles dispersed in a liquid which will not settle out) to a gel (a dispersion of a liquid throughout a solid matrix). It is a long established process with the key controlling processing steps being sol formation and gelling, drying, curing and sintering. Starting materials used in the preparation of the sol are usually inorganic metal salts or metal organic compounds such as metal alkoxides. Typically, the precursor is subjected to a series of hydrolysis and polymerization reactions to form a colloidal suspension. This suspension can be further processed to make materials in different forms from thin films and aerogels to nanocomposites and nanoparticles. The advantages of the process are perceived to be (i) low processing temperatures (ii) high homogeneity and purity of products and (iii) versatility with respect to the materials that can be formed. The sizes of nanoparticles produced by this method are 5–30 nm (Walt, 1997). In particular sol gel processing offers unique opportunities to generate gels of organic- inorganic materials (Sakka et al., 2003). The majority of sol-gel focus has been on producing glass ceramic powders, coatings and thin films. The increasing interest for these methods is that particles of high purity, controlled particle size and new composition may be produced. Particles of interest range from alumina, zirconia, titania and silica to titanates, phosphors, pigments and encapsulated pigments, optical materials, ferroelectrics and catalyst supports.

The new generation of sol-gel produced hybrid materials was initiated by the preparation of non-crystalline organic–inorganic materials. The physical and mechanical properties of these materials can be tailored by manipulating the ratio of inorganic–organics component. Resultant ‘super-repellent’ surfaces are based on a physical structure rather than chemical character (Scmidt et al., 2000.). Another new group is biological composite; an organic dye could be

entrapped in a porous silica cage led to the greater aspiration of incorporating biologically active materials in inorganic matrices to control reactions arising from the transport of materials in or out of the matrix (Uhlmann et al., 1998). In forming sols it is desirable to achieve a homogeneous colloid matrix. Material properties (including particle size) may be controlled by pre-reacting the slower reactive components or chelating the faster components to achieve homogeneity. Mechanical treatments and the use of ultrasound to generate a more homogeneous distribution of the nucleation sites for nanoparticles have been used. The drying stage is perhaps the most critical in influencing the properties of the final product (especially in catalyst supports, films and coatings). Past difficulties with shrinkage and cracking of coatings have to a significant degree been overcome with the use of drying control chemical additives (such as formamide) (Walt, 2002).

1.4.6 Microemulsion Methods

Recently Nanoparticles are used to prepare by microemulsion system. A microemulsion is a thermodynamically stable dispersion of two immiscible fluids; the system is stabilized by added surfactant(s) (Paul et al., 1997). In other wards Microemulsions are defined as homogeneous, optically transparent, and thermodynamically stable mixtures of oil and water stabilized by surfactants (Danielsson et al., 1981) Surfactant is a molecule that posses both polar and non-polar moieties. In water or oil solution, it dissolves and exists as monomer. The molecule of emulsifier associates spontaneously to form aggregates, called micelles. Micelles are responsible for many processes to enhance the solublization property of organic compound in water (o/w emulsion) hydrophilic compound in the oil phase (w/o emulsion).

There are three microemulsion systems. They are Winsor 1, Winsor 2 and Winsor 3. (Winsor et al. 1954) (1) Winsor 1 is also called as water in oil microemulsion (W/O), where water is dispersed in a hydrocarbon based continuous phase, and is normally located towards the oil apex of a water/oil/surfactant triangular phase diagram. (2) Winsor 2 is called as oil in water. (O/W), where oil is dispersed phase and water is continuous phase. (3) In Winsor 3, both water and oil is in same ratio. Both are movable. In addition to single-phase microemulsions, several phase equilibrium are known, namely Winsor systems (Rico et al., 1987)

Water-in-oil (w/o) microemulsions, or reverse micelles, are widely used for the preparation of a variety of nanoparticles due to their ability to efficiently mix reactants in their nanosize water pools, providing a highly homogeneous product with specified sizes stabilized by a surfactant layer. In this emulsion hollow particles are formed in aqueous phase. The small water pools act as a nonreactor, inside which particles are formed. The particles obtained in this system are generally very fine and monodisperse (Paul et al., 1997).

Microemulsion consists of at least, a ternary mixture of water, a surfactant or a mixture of surface- active agents and oil. Depending on the proportion of suitable components and hydrophilic-lypophilic balance (HLB) value of the surfactant used, the formation of micro droplets can be in the form of oil-swollen micelles dispersed in the aqueous phase as for the o/ w microemulsion or water-swollen micelles dispersed in oil as the w/o microemulsion. In addition to single-phase micro emulsions, several phase equilibrium are known, namely Winsor systems (Chadda et al., 1991).

REFERENCES

Burton W.K., and Cabrera N., Disc. Furaday SOC. 5, 1949, 33

Chadda, S., Ward, T.L., Carim, A., Kodas, T. T., Ott, K. and Kroeger, D., **"**Synthesis of $YBa_2Cu_3O_{7y}$ and $YBa_2Cu_4O_8$ by aerosol decomposition". *J. Aerosol Sci*., 22, 1991, 601.

Chung, Y.S., J. S. Lim, S.B. Park, and K. Okuyama, **"**Templated synthesis of silica hollow particles by using spray pyrolysis". *J. Chem. Eng. Jpn*., 37, 2004, 1099

Danielsson, I. and Lindman, B., "The definition of microemulsion" *Colloids Surf*., **3** 1981, 391–392.

Linyong, S., Xuewu, G., Mozhen, W. and Zhicheng, Z., "Direct preparation of silica hollow spheres in water in oil emulsion system: The effect of pH and viscosity". *J. Non-Crys. Solids*, 352, 2006, 2230.

Paul, B.K., and Moulik, S.P., "Uses and applications of microemulsions". *J. Dispersion Sci. Technol*., 18, 1997, 301.

Rico, I., Savignac, A. de, Samii, A. and Lattes, A., "Formamide, a water substitute in micelles and microemulsions: structural analysis using a Diels-Alder reaction as a chemical probe". *Tetrahedron*, 43, 1987, 1725

Scmidt, H., Jonschker, S., Goedicke, S. and Mennig, M. "The Sol-gel process as a basic technology for nanoparticle-dispersed Inorganic-organic composites". *J. Sol-Gel Sci. Technol.*, 19, 2000, 39–51.

Sakka, S., "Sol-Gel technology as Reflected in the Journal of Sol-Gel Science and Technology". *Journal of Sol-Gel Science and Technology*, 26, 2003, 29–33.

Uhlmann, D.R., and Teowee, G., "Sol-Gel Science and Technology: Current State and Future Prospects". *J. Sol-Gel Sci. Technol.*, 13, 1998, 153–162.

Walt, D., Nanomaterials. “Top-to-bottom functional design”. *Nature Materials*., 1, Sept. 2002, 17–18

Whitesides, G. M., and Love, J. Christopher, “The Art of Building Small”, 285 Sci. Am 2001, 39.

Whitesides, G. M., “Unconventional Methods For Fabricating and Patterning Nanostructures”. *Chem. Rev*., 99, 1999, 1823

Winsor, P. A., “Solvent Properties of Amphiphilic Compounds”, Butterworth, London, 1954.

Chapter-2

Literature Review

2.1 Introduction

Spherical polymeric micro- and nanomaterials serve as useful constructs due to their ease of synthesis, which can yield particles that possess a number of functional groups. Among these materials core-shell and hollow nanoparticles have attracted considerable research attention due to their large variety application in chemistry, biotechnology, medical science and material science. The core-shell nanoparticles are very common now due to its wide application. This is used as template of shell material. The overall process is a two or three step method; first, core is prepared in-situ or core material is supplied from outside, second, the core is coated with the shell material, third, removal of core to get hollow particle. The synthesis of core-shell depends on the material and methods. Sometimes core and shell is prepared separately and in some case simultaneously core and shells are prepared.

There are various core-shell nanoparticles have been synthesized. The metallic core and inorganic-shell nanoparticles is one of them. Silica can be used as shell material due to its specific properties like (A) inert to environment and systems and good stability (Liz-Marzan et al.1996), (b) biocompatible, (c) Fluorescent active (Kumar et al. 2006). The metal nanoparticles (e.g., Au and Ag) stems from their characteristic surface plasmon resonance (SPR), which influences linear and nonlinear optical properties when metal nanoparticles are irradiated by a light source (Scalisi et al. 2004). SPR characteristics are deter-mined by physical parameters of the metal fraction in a host matrix, such as silica (Wang et al. 2002). Nanoscale silver halide is getting increasing attention day to day due to its promising applications in the field of semiconductor (Zhiyun et al. 2005), antibacterial activity (Sambhy et al. 2006; Elahifard et al. 2007), photographic materials (Jeunieau et al. 2000) etc. So the silica coating on the nano metal core is a challenge to produce desired size and shape the core-shell nanoparticles

Fan et al. successfully synthesized self-assembled Au nano-particles in a silica matrix using a water-soluble nanoparticle micelle (Fan et al. 2004). They reported that Au nanoparticles dispersed in organic solvent could be readily transferred to an aqueous solution by surface modification of Au nanoparticles using a water-soluble surfactant. Similarly Kim et al also synthesized silica-coated Ag nanoparticles using a water-soluble nanoparticle micelle under basic conditions. Monodispersed Ag nanoparticles with a mean particle size of 7 nm were synthesized using $AgNO_3$ in the presence of ascorbic acid as a reducing agent (Kim et al. 2008).
The hollow nanoparticles are prepared from core-shell nanoparticle. They used core material as a template. The nano size hollow spheres were synthesized by removing core from shell structures (Teng et al. 2004; Song et al. 2003) by addition of chemicals like toluene, Conc. HF or HNO_3. Some core materials requires harass conditions for removing like solvent treatment followed by calcinations (Khanal et al. 2007) or heating in high temperature followed by solvent treatment (Le et al. 2004(b)).

2.2. Types of core: In some method, the core was prepared and then shell is coated over the core materials or core-shell is simultaneously formed. The core particles and shell are formed step by step. Then core particles are removed by simple solvent treatment or by taking some harass condition and some cores are self sacrificial. Generally core-shell method is common chemical method for preparing hollow metal nanoparticles. The templates used mainly include silica colloids (Stewart et al. 1999; Kramer et al. 2004; Schartl et al. 2000), polystyrene colloids (Agger et al. 1998), selenium colloids (Corma et al. 1997), silver nanoparticles (Sun et al. 2002), ceramic hollow spheres (Chah et al. 2002), and microemulsion droplets (Zhang et al. 2002).

4. Core removal Methods: Depending on the removal technique of the core materials, it can be broadly divided in to three categories as i) sacrificial template, ii) hard template and iii) Soft template.

The nano size hollow sphere are synthesized by using different templates to fabricate core shell structures including liquid crystals (Linyong et al. 2006), liquid droplets (Braun et al. 1999), micelles (Jiang et al. 2002), polymer particles (Huang et al. 1999; Shiho et al. 2000; Kawahashi et al. 1991; Eiden et al. 2002; Neves et al. 2002) or even inorganic compound nanoparticle (Tamai et al. 2000; Caruso et al. 1998).

2.2.1 Sacrificial template

In this methods the template its self sacrifice by dissolving in the solvent or high temperature treatment. It can be divided into two types as: self-templated and self-aggregation approaches. The self-aggregation is not as well understood as the former as it usually involves a less obvious formation mechanism. For example, SnO_2 hollow octahedral, in a significant fraction, are observed in the precipitate after hydrothermally heating a water/2-ropanolsolution containing SnF_2 and ethylenediamine at 180ºC, (Yang et al. 2004) during which some unidentified intermediate crystals might act as the quasi-templates.

2.2.2 Soft core:

Soft core can be removed by chemical reaction with reagents where as hard core requires harass condition like calcinations. Commonly used soft templates, including emulsion droplets, surfactant and other supramolecular micelles, polymer aggregates/vesicles, and gas bubbles.

Emulsion Methods: - When two immiscible liquids are mixed together through mechanical agitation (e.g., shaking, stirring), liquid droplets of one phase can be dispersed in the other continuous phase, forming an emulsion. Emulsions are thermodynamically unstable, thus surfactants or amphiphilic polymers, which self-assemble at the interface between the droplets and continuous phase, are required to increase kinetic stability. (Zimmermann et al. 2007) Oil-in-water (O/W) or water-in-oil (W/O) emulsions is most commonly employed. It should be noted that emulsion polymerization, where the droplets act as micro reactors, has long been used to synthesize solid and hollow polymer spheres. (McDonald et al. 2006).

2.2.3. Polymer compound using as core particles.

The polystyrene latex particles were used widely as template to prepare hollow particles (Jiang et al. 2002; Huang, et al. 2000; Tamai et al. 2000). The core-shell microspheres were prepared by dispersion polymerization (Wang et al. 2002) emulsion, miniemulsion and atom transfer radical polymerization (Sertchook et al. 2003; Xavier et al. 2002; Tiarks et al. 2001; Perruchot et al. 2001). The different types of polymeric materials are taken as core shell. Bourgeat-lami et al. (1998) prepared silica-polystyrene (SiO_2-PS) core-shell microspheres by dispersion polymerization (Xavier et al. 2002). These polymer materials like PS, PMMA etc. are more stable as core shell. But they can be easily removed either by calcinations or by dissolution (He et al. 2004). Some cores require strong acid (HF/ HNO_3) or harsh conditions (He et al. 2004; Xun et al. 2001).

Preparation of PS sphere using seed mediated method involves dissolution of a monomer in suitable medium, in the presence of emulsifier and initiator. Polymerizations of monomer start when the initiator decomposes to form nuclei. The nuclei grow to form polymer spheres. PS

Spheres are synthesized using styrene as a monomer, sodium styrene sulphaonate as an emulsifier and potassium persulphate as initiator. Sodium bisulphate and sodium bicarbonate act as buffer and reaction is carried out in inert atmosphere. (Zhang et al. 2006) Using this method, monodispersed spherical particles of size from 1 to 5 mm can be prepared.

B.Yang and coworker was synthesized hollow sphere by removing PMMA core shell. They prepared of 131–225 nm silicapolymethyl methacrylate (SiO_2-PMMA) core shell nanoparticles (CSNs) with 51–195 nm cores by an emulsion polymerization. The effects of several reaction parameters on the morphologies and sizes of SiO_2-polymer core shell nanoparticles has been studied, such as, different monomers (MMA and St), concentration of emulsifier, amounts of grafted silica and monomer.

Tetraethyl orthosilicate (TEOS), absolute ethanol and ammonium hydroxide were analytical grade and used as received. 3-(trimethoxysilyl) propyl methacrylate (MPS), styrene (St) and methyl methacrylate (MMA) were distilled under reduced pressure before used. 4, 4-isopropylidenediphenol bimethacrylate (BVA) was used as cross-linker and prepared in their laboratory. Potassium persulfate ($K_2S_2O_8$) and other agents of analytical grade were utilized without further purification. Deionizedwater was applied for all polymerization and treatment processes. The polymerization was then carried out in an atmosphere of nitrogen at 80 °C for 10 h, and then the product was centrifuged by various speeds and time according to the different sizes to remove the PMMA nanospheres without SiO_2 (for example, 159 nm SiO_2-PMMA CSNs with 111 nm cores were centrifuged by 15000 rpm for 6 min). SiO_2-PMMA CSNs were obtained. Solvent filled hollow polymer nanospheres were obtained after dissolving the SiO_2 cores using hydrofluoric acid (HF) as the etching solvent.

2.3 Conclusion

The core/shell nanoparticles have been classified in above. There are different core/shell materials available. We found from literature that silica has a wide application in real life and it has more stable and inert. There are many methods are available for synthesis of core/shell composites. The template assist method is simpler one. But for particularly silica nanoparticles Stöber method is very useful and isolation of particles is easy.

2.4 Motivation and objective of the methods

Although many different methods are available for synthesis of core/shell nanocomposites, the surface modification of core materials by chemical agent or surfactant are simple methods and very efficient. In this work we used surfactant for surface modification of core (AgBr) nanoparticle. The surface charge will be change. So the shell material will be coated on it because of opposite surface charge on the surface. In this method separation and isolation of core/shell composite will be easy.

The specific objectives of the project are:

1) To study growth kinetics, different parameters on equilibrium particle size of sliver bromide (AgBr) nanoparticles in both aqueous and surfactant media as a core.
2) To prepare silica nanoparticles by modified Stöber methods and study of different parameter affecting particle size.
3) To prepare core/shell nanoparticles, where silica as shell material and silver bromide as core material.

2.5 Organization of thesis

This thesis has been organized into six chapters. The chapter-1 contains introduction. The chapter-2 contains literature review of core/shell nanoparticles and type of core available for preparation of hollow nanoparticles. Here we focused particularly on silica nanoparticles as shell materials. Chapter-3 represents the synthesis and characterization of core AgBr nanoparticles. The growth kinetics of silver bromide nanoparticle has been studied in this chapter. Chapter-4 represents the synthesis and characterisation of silica nanoparticles, which can used as shell materials, by modified Stöber methods. In this chapter we studied how size of silica nanoparticles affected by different parameter and due to surfactant template. Chapter-5 represents the preparation and characterization of AgBr/silica core/shell nanoparticles. Finally chapter-6 concludes the research work which has been carried out and little suggestion for future work.

REFERENCES

Agger, J. R., Anderson, M. W., Permble, M. E., Terasaki, O. and Nozue, Y., "Growth of quantum-confined indium phosphide inside MCM-41". *J. Phys. Chem. B,* 102, 1998, 3345.

Caruso, F., Caruso, R. A. and Mohwald, H., **"**Nanoengineering of inorganic and hybrid hollow spheres by colloidal templating". *Science,* 282, 1999, 1111.

Eiden, S., and Maret, G., "Preparation and characterization of hollow spheres of rutile". *J. Colloid Interf. Sci*., 250, 2002, 281.

Elahifard, M. R., Rahimnejad, S., Haghighi, S. and Gholami, M. R., "Apatite-coated Ag/AgBr/TiO_2 visible-light photocatalyst for destruction of bacteria". *J. Am. Chem. Soc.* 129 (31), 2007, 9552.

Fan, H.Y., K. Yang, D.M. Boye, T. Sigmon, K.J. Malloy, H.F. Xu, G.P. Lopez, C.J.Brinker, Self-assembly of ordered, robust, three-dimensional gold nanocrystal/silica arrays, *Science* 304, 2004, 567.

He, G., and pan, Q., "Synthesis of polystyrene/ poly (methyl methacrylate) nanoparticles. Macromol". *Rapid Commun.* 25, 2004, 1545-1548.

Huang, H., Remsen, E.E., Kowalewski, T. and Wooley, K. L., "Nanocages derived from shell cross-linked micelle templates". *J. Am. Chem. Soc*., 121, 1999, 3805.

Huang, J., Xie, Y., Li, B., Liu, Y., Qian, Y. and Zhang, S., "In-situ source-template-interface reaction route to semiconductor CdS submicrometer hollow spheres." *Adv. Mater*., 12, 2000, 808.

Jiang, X., Xie, Y., Lu, J., Zhu, L., He, W. and Liu, X., "Low temperature interface-mineralizing route to hollow CuS, CdS, and NiS spheres". *Can. J. Chem*., 80, 2002, 263**.**

Jeunieau, L., Verbouwe, W., Rousseau, E., Auweraer, van der M., and Nagy, J.B., "Interaction of an oxa- and thiacarbocyanine dye and silver halide nanoparticles synthesized in a microemulsion system**"**. *Langmuir* 16**,** 2000, 1602.

Kawahashi, N., and Matijevic, E., "Preparation of hollow spherical particles of yttrium compounds", *J. Colloid Interf. Sci*., 143, 1991, 103.

Khanal, A., Inoue, Y., Yada, M. and Nakashima, K., "Synthesis of silica hollow nanoparticles templated by polymeric micelle with core-shell-corona structure". *J. Am. Chem. Soc.*, 129, 2007, 1534.

Kim, Soon-Gil, Nobuhiro Hagura, Ferry Iskandar, Kikuo Okuyama, Characterization of silica-coated Ag nanoparticles synthesized usinga water-soluble nanoparticle micelle. *Adva. Powder Tech*. 20, 2009, 94.

Kumar A, Pushparaj V. L, Murugesan S, Synthesis of silica-gold nanocomposites and their porous nanoparticles by an in-situ Approach. *Langmuir* 222, 2006, 8631.

Le, Y., Chen, J. F., and Wang, W. C., "Study on the silica hollow spheres by experiment and molecular simulation". *Applied Surface Sci*., 230, 2004, 319

Linyong, S., Xuewu, G., Mozhen, W. and Zhicheng, Z., "Direct preparation of silica hollow spheres in water in oil emulsion system: The effect of pH and viscosity". *J. Non-Crys. Solids*, 352, 2006, 2230.

Liz-Marzan L.M., M. Giersig, P. Mulvaney, *Langmuir* 12, 1996, 4329

McDonald, C. J., Bouck, K. J., Chaput, A. B. and Stevens, C. J., "Emulsion polymerization of voided particles by encapsulation of a nonsolvent". *Macromolecules*, 33, 2000, 1593.

Neves, M. C., Trindade, T., Timmons, A. M. B. and Pedrosa de Jesus, J. D., "Synthetic hollow zinc oxide microparticles". *Mater. Res. Bull*., 36, 2001, 1099.

Pellegri, N., R. Trbojevich, O. De Sanctis, K. Kadono, Fabrication of PbS nanoparticles embedded in silica gel by reverse micelle and sol–gel routes, *J. Sol–Gel Sci. Technol*. 8, 1997, 1023.

Perruchot, M.A. Khan, A. Kamitsi, and Armes, S. P., "Synthesis of welldefined, polymer-grafted silica particles by aqueous ATRP". *Langmuir*, 17, 2001, 4479–4481.

Philipse, A.P., M.P.B.C. van Bruggen, Magnetic silica dispersions: preparation and stability of surface-modified silica particles with a magnetic core, *Langmuir* 10, 1994, 92.

Sambhy, V., MacBride, M., Peterson, B. R. and Sen, A., 'Silver bromide nanoparticle/polymer composites: dual action tunable antimicrobial materials". *J. Am. Chem. Soc.* 128 (30), 2006, 9798.

Scalisi, A.A., G. Compagnini, L. D'Urso, O. Puglisi, Nonlinear optical activity in Ag–SiO_2 nanocomposite thin films with different silver concentration, *Appl.Surf. Sci*. 226, 2004, 237.

Sertchook, H., Avnir, D., "Submicron silica/polystyrene composite particles prepared by a one-step sol–gel process", *Chem. Mater*., 15, 2003, 1690–1694.

Shiho, H., and Kawahashi, N., "Iron compounds as coatings on polystyrene latex and as hollow spheres". *J. Colloid Interf. Sci*., 226, 2000, 91.

Tamai H., Ikeya, T., Nishiyama, F., Iida, K. and Nojima, S.,"NO decomposition by ultrafine noble metals dispersed on the rare earth phosphate hollow particles". *J. Mater. Sci*., 35, 2000, 4945.

Tiarks, F., Landfester, K. and Antonietti, M., "Silica nanoparticles as surfactants and fillers for latexes made by miniemulsion polymerization", *Langmuir*, 17, 2001, 5775–5780.

Wang, T.C., R.E. Cohen, M.F. Rubner, Metallodielectric photonic structure based on polyelectrolyte multilayer's, *Adv. Mater*. 14, 2002, 1534.

Xavier-L., J., Guyot, A. and Bourgeat-Lami, E., "Synthesis and characterization of silica/poly (methyl methacrylate) nanocomposite latex particles through emulsion polymerization using a cationic Azo initiator". *J. Colloid Interface Sci*., 250, 2002, 82–92.

Xun, F., Lin, L., Debao, W., Zhengshui, H. and Ying, M., "Amino acid extraction with AOT reverse micelle". *Colloids Surface A*., 179, 2001, 1-10.

Yang, H. G., and Zeng, H. C., "Self-construction of hollow SnO_2 octahedra based on two dimensional aggregations of nanocrystallites". *Angewandte Chemie*, 43, 2004, 5930.

Zhiyun, C., Fleet Erin, F. and Cooper G., "Applications of semiconductor nano-sized particles for photolithography". PATENT US007524616B2, 2009.

Chapter-3

Synthesis and characterization of silver bromide nanoparticles in aqueous surfactant solutions

3.1 Introduction

The nano sized materials have a great interest in the field of science and technology due to their superiority in different properties such as physical, chemical, electronic, optical, etc. over the bulk scale material. Nanoscale silver halide is getting increasing attention day to day due to its promising applications in the field of semiconductor (Zhiyun et al., 2009), antibacterial activity (Sambhy et al.,2006, Elahifard et al., 2007) photographic materials (Sturmer et al., 1989, Jeunieau et al., 2000), and for adsorption study of dyes (Jeunieau et al., 2000) etc.

Although there are many studies available on the preparation of silver halide nanoparticles (Husein et al., 2000, 2003, 2004, 2005, 2006, 2007, Oleshko et al., 2008) but there are limited studies on kinetics of particle formation (Spirin et al., 2008, Hasse et al., 2006). The studies on kinetics of particle formation can give us important information about the nucleation and growth of the particles. Among the above studies mostly microemulsions are used as nanoreactor to control the particle size. Husein et al. (Husein et al., 2003, 2004) have prepared silver chloride and bromide nanoparticles in the microemulsion method using dioctyldimethyl ammonium chloride, dioctyldimethyl ammonium bromide, and cetyltrimethyl ammonium bromide cationic surfactants. In these methods surfactants counter ion is used as a source of halide ion to get silver halide. They have also prepared AgCl and AgBr nanoparticles in the presence of microemulsions containing cationic surfactants dioctyldimethylammonium chloride and cetyltrimethylammonium bromide from the respective solid powder of AgCl and AgBr (Husein et al., 2005, 2006). Spirin et al. (Spirin et al., 2008) have studied the growth kinetics of AgI nanoparticles in AOT reverse microemulsion using different chain length oil phase (*n*-hexane, *n*-octane, *n*-decane, *n*-dodecane). They found if the water/surfactant molar ratio (W) is low (~2) there was no change in particle size by changing the chain length of oil phase but there

is a significant change at higher value of W. In addition, lower particle size was obtained when the oil chain length was low. From the literatures it has been found that there is no study available growth kinetics of silver bromide nanoparticles in aqueous media and in the presence of different aqueous surfactant solutions.

In this study, we investigated the growth kinetics of silver bromide nanoparticles in aqueous solution in the presence of surfactants. Different parameters such as reactant ($AgNO_3$) concentration, surfactant concentration, temperature of the medium on growth kinetics have also been studied here. There are only limited studies are available of the growth kinetics of AgBr nanoparticles and to the best of our knowledge similar studies are not available in the literature.

3.2 Experimental Section

3.2.1 Materials

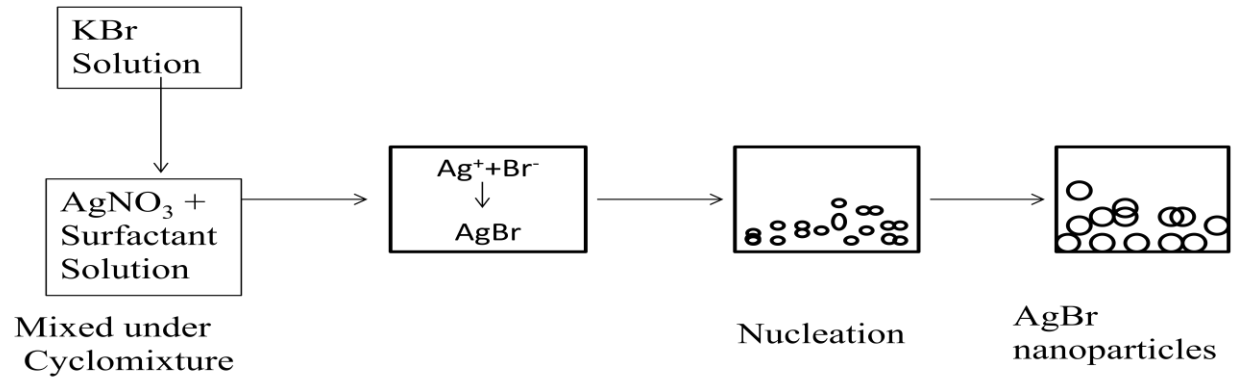
The reagent grade silver nitrate (99.9 %), potassium bromide (99.3 %) were purchased from Rankem, India, The surfactant Triton X-100 (TX-100, Laboratory grade, Cat no. 9002-93-1) from Sigma-Aldrich, Germany, was used without any further purification. Ultra pure water of 18.2 MΩ.cm resistivity and pH 6.4 – 6.5 (Sartorius, Germany) was double distilled again and used for all the experiments.

3.2.2 Methods

The silver bromide nanoparticles were prepared by simple precipitation reaction of silver nitrate with potassium bromide. Fresh silver nitrate solution was prepared and used for each experiment to avoid photo oxidation of $AgNO_3$ solution. In the absence of surfactants, $AgNO_3$ solution was added to potassium bromide solution under mixing condition using a cyclomixer to get AgBr nanoparticles in the aqueous solution. In the presence of surfactant, potassium bromide and surfactant solutions were mixed, and then silver nitrate solution was added under the mixing

condition. The constant temperature of the solution was maintained throughout the experiment using a water bath circulator. All the solutions were sonicated before mixing for degasification; the sample was also sonicated in a sonication bath for ~ 1 min just before the particle size analysis. The particle size (diameter) was analyzed by dynamic light scattering (DLS) technique using a Malvern Zeta Size analyzer (Nano ZS, Malvern, U.K.). Dynamic light scattering (DLS) theory is a well established technique for measuring particle size over the size range from a few nanometers to a few microns.

The kinetics of particle formation was also studied spectrophotometrically using a UV-Vis-NIR spectrometer (UV-3600, Shimadzu, Japan). The instrument has a good facility to study the kinetics of particles formation. The λ_{max} value of the particular particles has given and it is plotted a graph of absorbance vs. time (min), which will show in the screen. The particle shape and size was observed under a SEM (JEOL, JSM-6480LV). The sample was prepared using metal plate and it is coated with platinum for better conductance of electricity. The particles were also characterized by using Philips (PW 1830 HT) X-ray diffractometer with a scanning rate 0.05 θ /sec. The particles taken in powder form and X-ray carried on using the powder.



Schematic diagram-1. The synthesis of AgBr nanoparticles.

3.4 Results and discussion

3.4.1 Effect of reactant concentration on equilibrium time and particle size

The rate of change of particle size with time or the growth kinetics is an important phenomenon in any nanoparticle synthesis process. The formation of equilibrium or final AgBr particle size may consists of two steps (i) precipitation reaction of silver nitrate and bromide ion to form nuclei and (ii) collision of nuclei or diffusion of molecules to the nuclei surface and deposited to form the final particle size. The first step is the reaction step followed by growth. The first step may be very fast, since the reaction rate is fast; as a result, the final particle size depends totally on the growth process. First we have studied the growth kinetics of AgBr particles in aqueous media with the variation of $AgNO_3$ concentration. The results presented in Figure 3.1a show the particle size gradually increases with time and ultimately reached to the equilibrium, and the equilibrium particle size increases with the decrease in reactant concentration among the three reactant concentrations studied here. Similarly, the equilibrium time also depends on the reactant concentration that decreases with the decrease in reactant concentration. It is observed that the saturation time for 0.01, 0.05, and 0.1 mM $AgNO_3$ are ~ 30, ~ 55, and ~ 60 min respectively. Moreover, 60–70 % of the equilibrium size is achieved within 10 min and after that there is a slow increase in size for all three concentrations. The particle size distributions are also shown in Figure 3.1b, clearly indicates at lower reactant concentration the distribution is wide. The growth kinetics studied by UV-Vis spectroscopy also shows similar trends with some differences in equilibrium time as shown in Figure 3.2. The change in absorbance is very significant among the three different reactant concentrations studied here. The equilibrium time are in UV-Vis spectroscopy studies are ~ 20, ~ 50, and ~ 70 min for 0.01, 0.05, and 0.1 mM concentrations respectively at a constant wavelength of 270 nm. Although there are some similarities between UV and DLS results still the study was carried out using UV-Vis spectroscopy, as the nucleation step is very fast and it is difficult to study the change in size at lower time scale using DLS. The UV results presented in Figure 3.2 show the sharp increasing absorption portion is due to nucleation, after that the growth process starts.

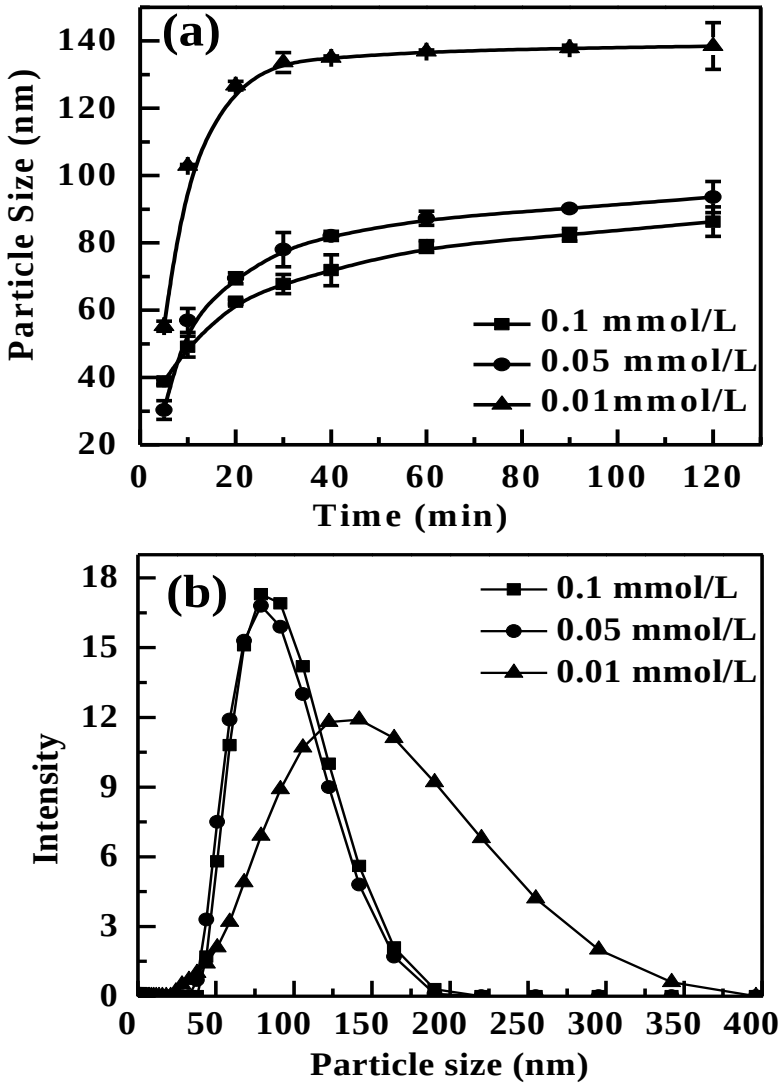


Figure 3.1. (a) The growth kinetics of AgBr nanoparticles using different reactant concentrations in aqueous media. (b) The distribution of AgBr nanoparticles.

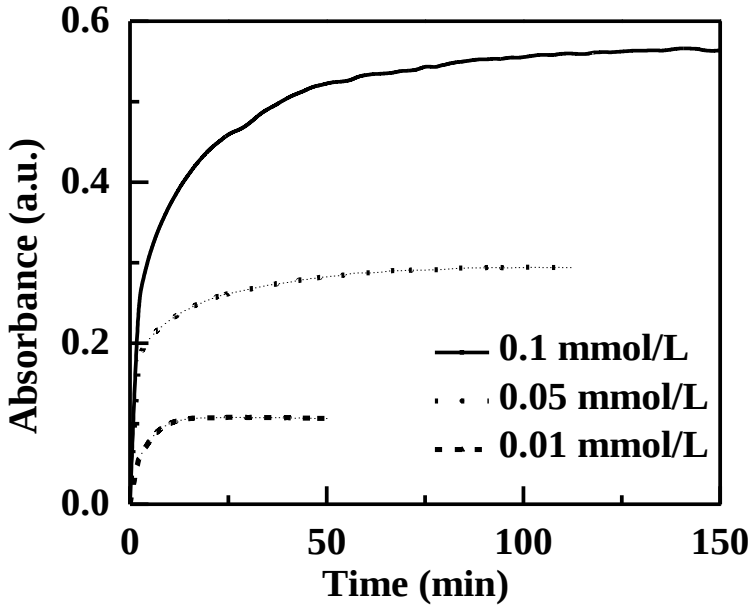


Figure 3.2. The growth kinetics of AgBr nanoparticles in aqueous media using different reactant concentrations by UV-Vis spectrophotometer at 270 nm wavelength.

It is well known that the reactant concentration plays a crucial role on the final particle size. In this study, the effect of reactant concentration on equilibrium particle size shows the particle size decreases with the increase in reactant concentration. The reported literature suggests that the change in particle size with increasing reactant concentration never follows a particular trend, whereas, increasing (Sugimoto et al., 2000, Mafune et al., 2000) or decreasing (Pal et al., 1997, Pawar et al., 2009) trends in particle size are found to be depended on the types of particles, synthesis media; in general, the increasing size is quite common. When there are more than one reactant is there, at low reactant concentration the number of nuclei formed will be less, may be due to slow reaction rate. The atoms (embryos) formed at the later period will collide with the already formed nuclei instead of formation of new nuclei, leading to the larger size particle. Whereas, when the reactant concentration is increased due to increase in reaction rate, formation of nuclei also will be more and the final particle sizes become low. More

specifically, the solubility of AgBr decreases in aqueous media, when the concentration of $AgNO_3$ is increased due to the presence of common ion (Ag^+). As a result, in the particle formation process as soon as the reaction is over embryo to nucleus transition became faster and favorable. Ultimately, due to formation of more nuclei the final particle sizes are low. The equilibrium particle sizes are 137±1, 90±2, and 83±2 nm for 0.01, 0.05 and 0.1 mM concentrations of reactant respectively obtained from the DLS data.

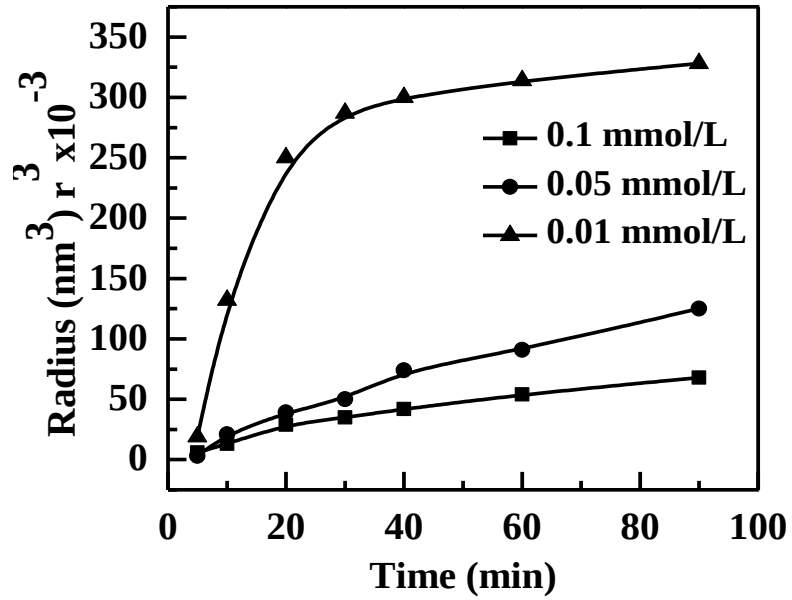


Figure 3.3. The plot of cube of the radius of AgBr particles vs. time prepared in aqueous media.

From the LSW model (Lifshitz, Slyozov, and Wagner) coarsening kinetics can be written as (Rao et al., 2007)

$$r_{av}^3 - r_0^3 = k_c t \qquad (3.1)$$

Where, r_{av}^3 and r_0^3 are the average and initial particle radius respectively, k_c is diffusion limited coarsening rate constant, and t is time. Figure 3.3 shows the plot of r_{av}^3 vs. time. The increasing

particle size at longer time is attributed to diffusion-limited coarsening. The rate constant (k_c) can be obtained from the slope of the equation 1 at the higher time scale. Figure 3.4 shows the plot of the coarsening rate constant vs. reactant concentration. The coarsening rate constant increases almost linearly with the increase in reactant concentration.

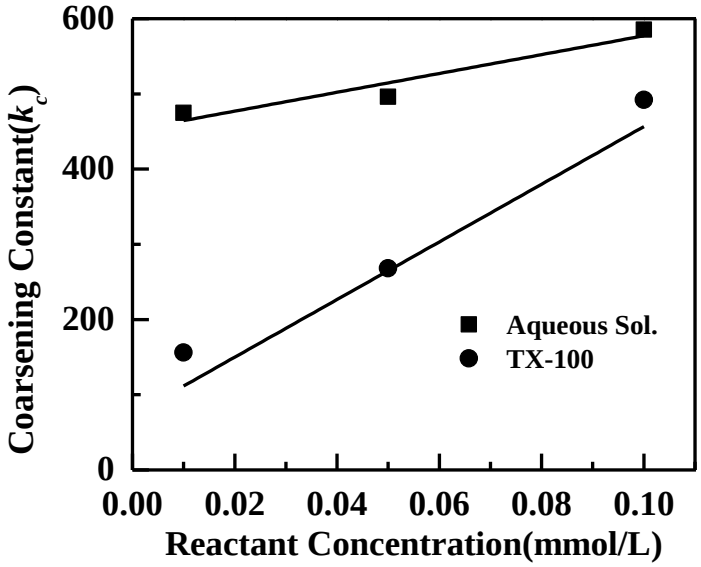


Figure 3.4. The plot of coarsening constant with the increasing reactant concentration in the pure aqueous and TX-100 media.

3.4.2 Effect of surfactant:

The nature of the surfactants and their structures are also greatly influenced the growth rate, equilibrium size, zeta potential, and stability of the particles. Here we have studied the effect of a nonionic surfactant (TX-100) on particle size and growth. The effect of reactant concentration was studied in the presence of TX-100 using concentrations 0.001, 0.01, 0.05, and 0.1 mM shown in Figure 3.5a. The concentration of the surfactant was used 0.45 mM (thrice the CMC).

Similar to the pure aqueous solution, it is observed that the particle size decreases with the increase in reactant concentration, and the overall particle sizes are lower than that of pure aqueous media. It can be clearly seen that the equilibrium particle size is lower in the presence of TX-100 than that of aqueous solution. The equilibrium time and particle sizes of AgBr in the presence and absence of surfactant at 0.01 mM $AgNO_3$ are shown in figure. The presence of nonionic surfactant TX-100 shows lower equilibrium particle size with less equilibrium time. Similar to the pure aqueous media the change in coarsening constant with reactant constant in the presence of TX-100 is plotted in Figure 3.4. The similar trend is also found for TX-100 media with the overall lower coarsening constant values. At higher reactant concentration the particle size distribution is also narrow as shown in Figure 3.5 (b).

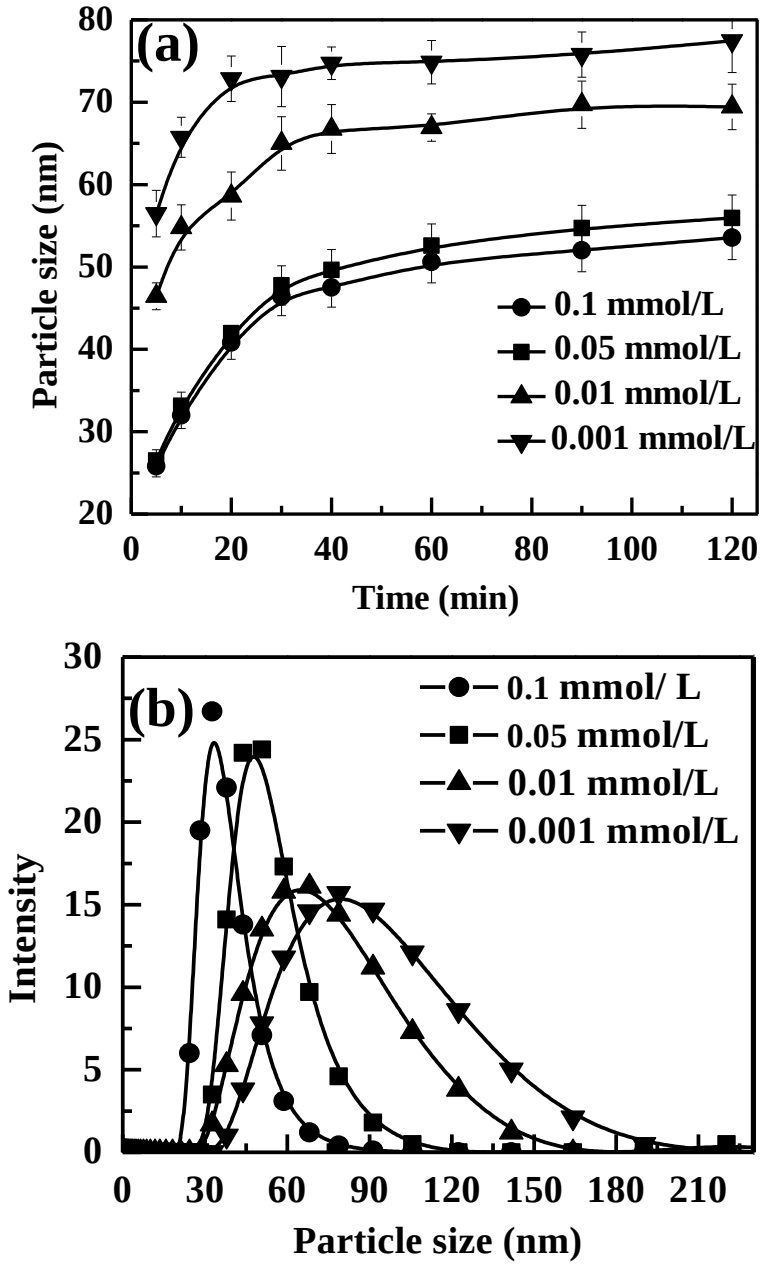


Figure 3.5. (a) The growth kinetics of AgBr particles in TX-100 media using different reactant concentrations. (b) The distribution of AgBr nanoparticles.

The effect of surfactant concentrations on the equilibrium particle size in a wide range, from below to above CMC was also studied and it is observed the presence of TX-100, the change in particle size is negligible with the change in surfactant concentration.

The kinetics of particle growth in the presence of surfactants was also studied using UV-Vis spectrophotometer. In the presence of surfactants the peak at maximum absorbance value changes to lower wavelength may be due to adsorption of surfactant. The distinct spectrum is obtained for the AgBr nanoparticle with a maximum absorbance at 238 nm wavelength in the presence of TX-100 solution. Figure 3.6 shows clearly that the absorbance value increases gradually with time and almost constant after 30 min using a constant $AgNO_3$ (0.1 mM) concentration. The reactant concentration effect was also studied using three different concentrations 0.01, 0.05, 0.1 mM $AgNO_3$ in the presence of TX-100 at 238 nm wavelength. The absorbance values increase gradually with time and finally reached to a plateau region at equilibrium, also there is an increase in absorbance value with the increasing reactant concentration. This can be attributed with the increase in reactant concentration particle size decreases; as a result increase in number of particles in the solution as well as the absorbance.

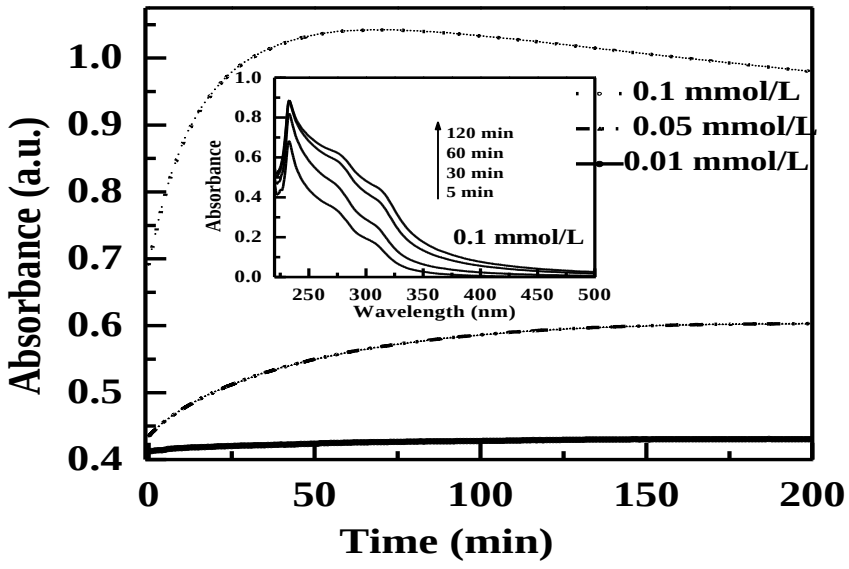


Figure 3.6. The growth kinetics of AgBr nanoparticles in TX-100 media using different reactant concentrations at 238 nm. Inset shows the full spectra at different time from 0.1 mM reactant concentration.

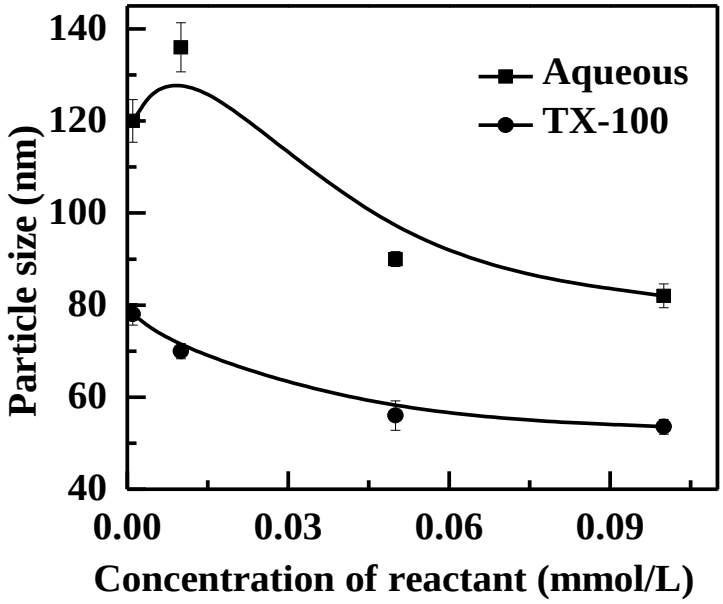


Figure 3.7. The change in equilibrium particle size of AgBr nanoparticles with the reactant concentration in pure aqueous and TX-100 media.

Figure 3.7 shows the change in equilibrium particle size with the reactant concentration in aqueous and surfactant media of surfactant concentration three times above their respective CMCs. In pure aqueous media at very low reactant concentration initially there is a little increase in particle size with the increase in reactant concentration, above 0.01 mM concentration there is a gradual decrease in particle size with the increase in reactant concentration. Whereas in the presence of TX-100 there is a gradual decrease in particle size is observed.

3.4.3 Effect of Temperature

The effect of temperature on the growth kinetics and equilibrium particle size was studied in aqueous media in the presence and absence of surfactant solutions ranging from 20 ºC to 40 ºC. Lower temperature was avoided due to decrease of solubility of the surfactants in aqueous

media. The effect of temperature on growth kinetics of silver bromide nanoparticles is shown in Figure 3.8. It is observed that in both the cases aqueous solutions with and without surfactants, the particle size and equilibrium time increases with the increase of temperature. The kinetic energy of the system increases with the increasing temperature, as a result the probability of collision between the nanoparticles also increases. The collisions between the particles enhance the growth rate and lead to formation of bigger size nanoparticles. In addition after the formation of nucleus, growth also proceeds due to diffusion of the molecules from aqueous phase to the nucleus surface. At higher temperature, growth rate increases due to increase in diffusion rate. Increase in temperature means an increase in molecules' speed (kinetic energy). So the molecules move faster and there will be more mixing of molecules, as a result, the rate of diffusion will be faster. The average molecular energy can be expressed as ~ exp(-E/kT). The collision between the particles in turn enhanced the growth rate and led to the formation of larger particles. In aqueous solution, there is a sharp increase in particles size with the increasing temperature from 20 to 30 ºC. Whereas, when the temperature is increased to 40 ºC there is no such change in the particle growth. However, in the presence of TX-100 between 20 and 30 ºC the change is not significant, but there is a significant difference with that of 40 ºC. This can be attributed as the surfactants are adsorbing on the particle surface the adsorbed surfactant layer resists collision between the particles but further increase the temperature to 40 ºC may favor collision, leads to increase in particle size.

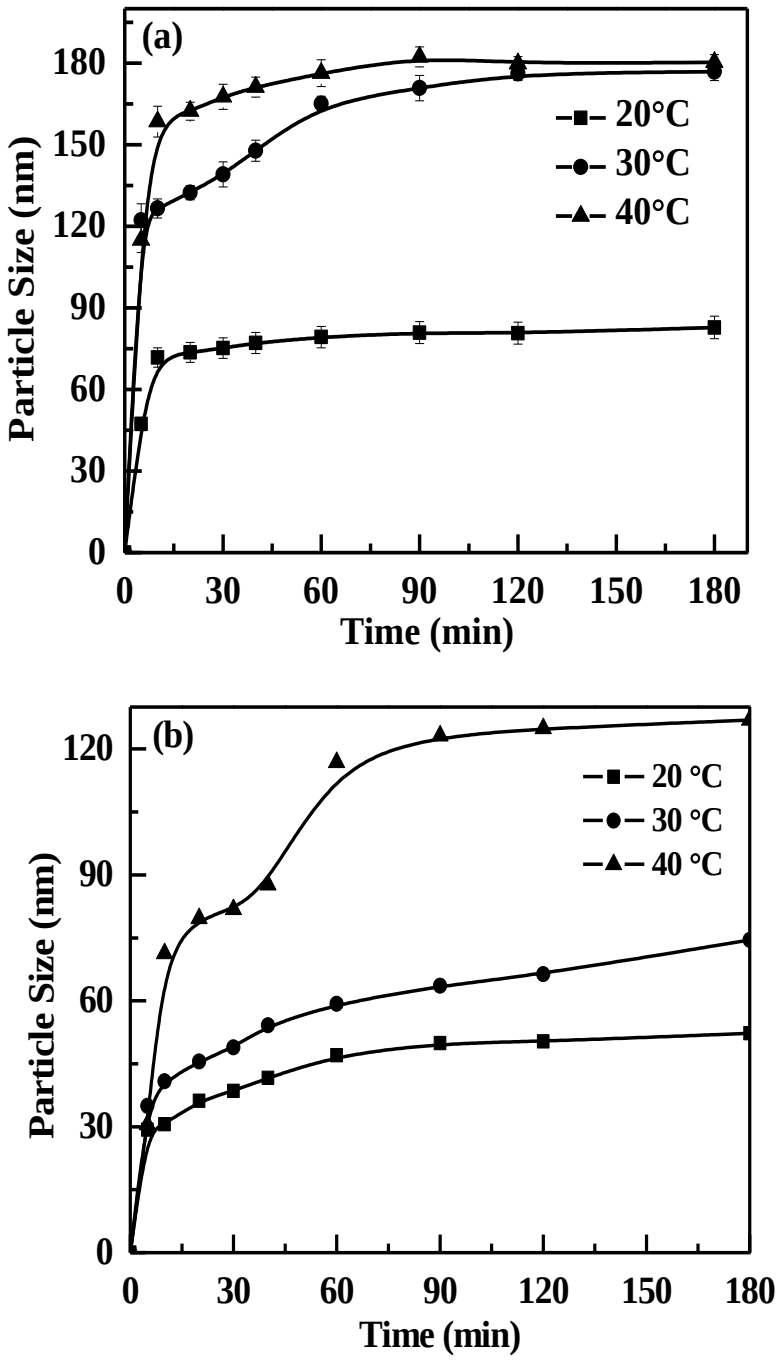


Figure 3.8. The growth of AgBr nanoparticles at different temperatures from 0.1 mM $AgNO_3$ concentration. (a) Aqueous media (b) TX-100 media.

According to Arrhenius equation the coarsening rate constant is again related to temperature and activation energy as

$$k_c = Ae^{-\frac{E_a}{RT}} \text{ or } ln\, k_c = -\frac{E_a}{RT} + ln\, A \qquad (3.2)$$

Where E_a is activation energy for the growth process, A is the constant, R is the universal gas constant, and T is the temperature (K). The activation energy of the coarsening process can be calculated from slope of $ln\ k_c$ vs. T^{-1} plot shown in Figure 3.9. The activation energy obtained from the figure is 83.29±3.4 kJ/mol for aqueous solution and 77.67±2.31 kJ/mol for surfactant solution. The activation energies obtained are comparable with the reported values of other hydrophilic particles such as TiO_2 (72.35 kJ/mol), (Oskam et al., 2003) ZnO (108.04 kJ/mol), (Hu et al., 2005) or Silicalite-1 (73.90 $\pm$ 2.80 kJ/mol). (Cheng et al., 2005)

The coarsening constant k_c can be also written as,

$$k_c = \frac{8\gamma D V_m^2 C_\infty}{9RT} \qquad (3.3)$$

Where γ is the surface energy of AgBr (J/m^2), D is the diffusivity of AgBr molecules (11×10^{-10} m^2/sec), V_m is molar volume (28.9 cm^3/mol) (Grammatikakis et al., 1992), C_∞ is AgBr concentration, R is universal gas constant (8.31 J/mol.K), and T is the working temperature (303 K). The bulk diffusivity of the silver bromide molecules can be calculated by using Stokes-Einstein equation, (Hiemenz et al., 1997)

$$D = \frac{k_B T}{6\pi\eta a} \qquad (4)$$

Where k_B Boltzmann constant (1.38×10^{-23} J/K), η is viscosity of the media (8.38×10^{-4} kg/m.s) (Terpilowski et al., 2008), and a is the hydrodynamic radius (0.264 nm) (Mariano et al., 1998) of AgBr molecule. The surface energy is 219, mJ/m^2 for the concentration of 0.01 mM of $AgNO_3$

concentration at room temperature. The calculated surface energy can be comparable with the range of the reported values by other authors' 91.5 - 188 mJ/m^2. (Sugimoto et al., 2001)

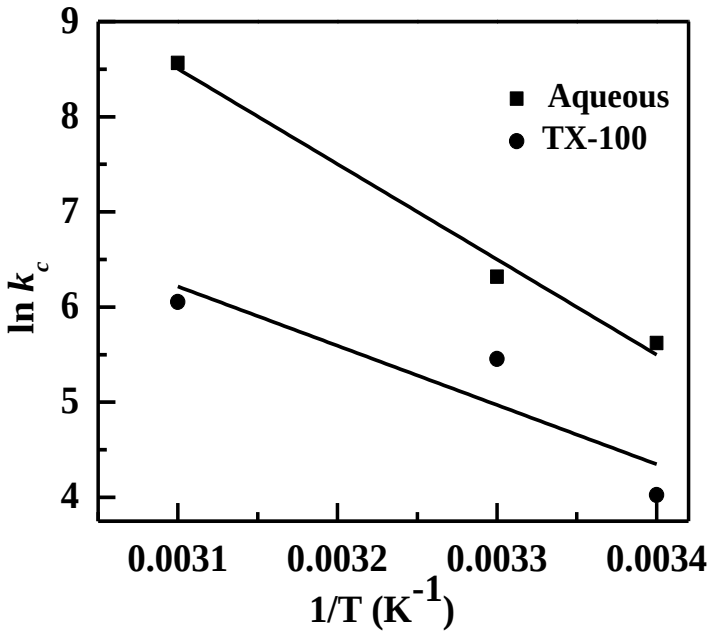


Figure 3.9. The plot of lnk_c vs. T^{-1} in pure aqueous and TX-100 media.

3.4.4 Particle characterization by XRD and SEM

The synthesized particles were also characterized by XRD and the pattern of the AgBr particles is presented in Figure 3.10. The peaks of XRD spectrum are clearly distinguishable. The XRD pattern of AgBr in both surfactant and aqueous media are displaying main three peaks located at 30.8°, 44.2°, and 54.9° corresponds to (200), (220) and (222) planes respectively (79-0149 from JPCDS PDF Number). The most intense peak is obtained at (200) plane. The peaks are comparatively slight narrow in surfactant media indicates more crystalline than the pure aqueous media.

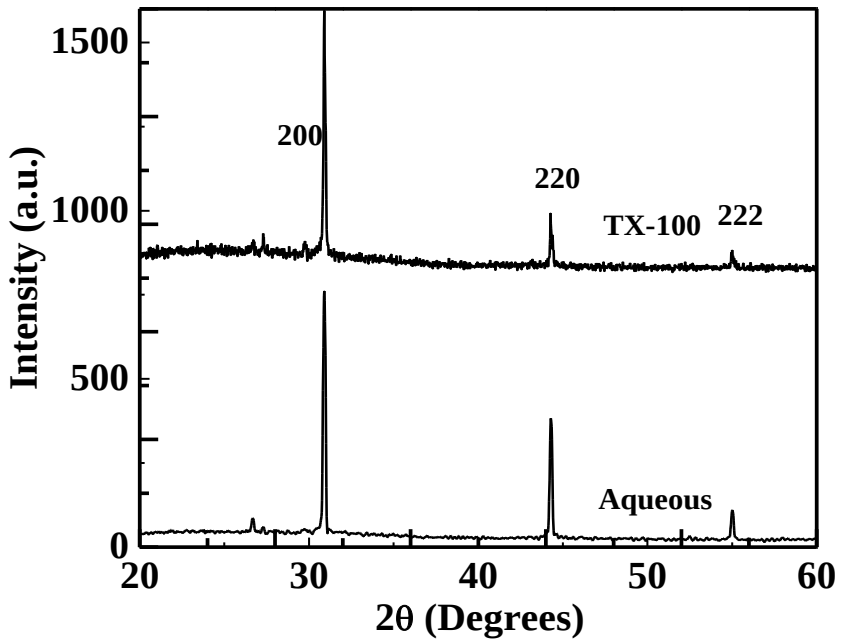


Figure 3.10. Powder X-ray diffraction pattern of AgBr in pure aqueous and TX-100 media.

The SEM images of AgBr nanoparticles using 0.01, 0.1 mM reactant concentration in pure aqueous media and 0.01 mM reactant concentration in the presence of TX-100 media are shown in Figures 3.11 a, b, c respectively. It can be clearly seen that the particles are mostly spherical in shape. The comparison between the Figures 3.11 a, b show with the increase in concentration from 0.01 to 0.1 mM there is a decrease in particle size as discussed before. The comparison between Figures 3.11 a, c also shows the presence of TX-100 generates smaller size particles than that of pure aqueous media. The particle size obtained by DLS in the presence of surfactant is larger than that by SEM may be due to the adsorbed surfactant layer as well as hydrated water molecules.

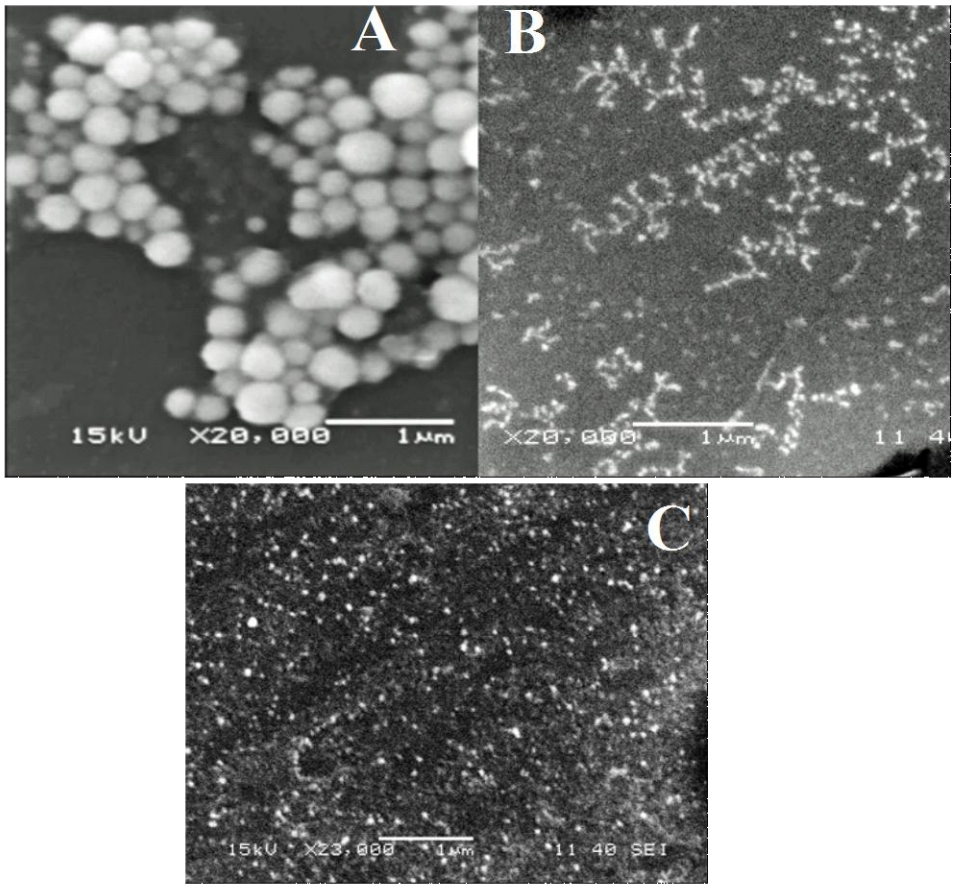


Figure 3.11. SEM images of AgBr nanoparticles (a) using 0.01 mM $AgNO_3$, (b) 0.1 mM $AgNO_3$ (c) 0.01 mM $AgNO_3$ in the presence of TX-100.

3.5. Conclusion

Although there are many studies available on the synthesis of AgBr nanoparticles, but those are mainly concentrated on microemulsion based method. In addition, those studies are mainly focused on the equilibrium size particles; limited studies are there on growth kinetics. This study focuses on the important parameters to control the particle size in the aqueous media. Since, AgBr

is an important material having many potential uses these results may be useful to generate small size particles in aqueous media.

The results can be summarized as follows:

Spherical size AgBr nanoparticles can be prepared in aqueous media in the absence and presence of surfactant. Lower size particles can be obtained in pure aqueous media by increasing the reactant concentration. The coarsening rate constant for the particle formation increases linearly with the increase in reactant concentration. The presence of nonionic surfactant generates smaller size of particles than the pure aqueous media. The temperature effect shows that in pure aqueous media there is an increase in particle size with the increase in temperature from 20-30 °C after that the change is not significant till 40 °C. Whereas, in the presence of TX-100 20-30 °C temperature range the change is not significant but further to 40 °C there is a significant change in size.

REFERENCES

Cheng, C. H., D. F. Shantz, *J. Phys. Chem. B* 109, 2005, 19116

Chen, D. H., Hsieh, C. H. "Synthesis of nickel nanoparticles in aqueous cationic surfactant solutions". *J. Mater. Chem.*, 12, 2002, 2412-2415.

Chen, S., Carroll, L.D., "Silver Nanoplates: Size Control in Two Dimensions and Formation Mechanisms". *J. Phys. Chem. B, 108,* 2004, 5500-5506.

Destrée, C., Nagy, and J. B., "Mechanism of formation of inorganic and organic nanoparticles from microemulsions." *Adv. Colloid Interface Sci*., 353, 2006, 123–126.

Elahifard, M. R., Rahimnejad, S., Haghighi, S. and Gholami, M. R., "Apatite-coated Ag/AgBr/TiO_2 visible-light photocatalyst for destruction of bacteria". *J. Am. Chem. Soc.* 129 (31), 2007, 9552–9553.

Glaus, Stephan and Calzaferri, G., 'The band structures of the silver halides AgF, AgCl, and AgBr: A comparative study**'.** *Photochem. Photobiol. Sci.* 2, 2003, 398–401.

Hamilton, J.F., "Physical properties of silver halide microcrystals". *Photographic Sc. and Eng*. 18 (5), 1974, 493–500.

Hasse U., Fletcher S. and Scholz F., "Nucleation-growth kinetics of the oxidation of silver nanocrystals to silver halide crystals". *J. Solid State Electro.* 10, 2006, 833–840.

Holmberg, K., Jonsson, B., Kronberg, B. and Lindman B., "Surfactant and polymer in aqueous solution." 2nd edition, *Willey Inter Science*. 2002, 48.

Husein, M. M., Rodil, E. and Vera, J. H., "A novel method for the preparation of silver chloride nanoparticles starting from their solid powder using microemulsions". *J. Colloid Interface Sci*. 288, 2005, 457–467.

Husein, M. M., Rodil, E. and Vera, J. H., "Formation of silver chloride nanoparticles in microemulsions by direct precipitation with the surfactant counter ion". *Langmuir* 19, 2003, 8467-8474.

Husein, M. M., Rodil, E. and Vera, J. H., "Formation of silver bromide precipitate of nanoparticles in a single microemulsion utilizing the surfactant counterion". *J. Colloid Interface Sci*. 273, 2004, 426–434.

Husein, M. M., Rodil, E. and Vera, J. H., "A novel approach for the preparation of AgBr nanoparticles from their bulk solid precursor using CTAB microemulsions". *Langmuir* 22, 2006, 2264-2272.

Husein, M. M., Rodil, E. and Vera, J. H., "Preparation of AgBr nanoparticles in microemulsions via reaction of $AgNO_3$ with CTAB counterion". *J. Nanopart. Res*. 9, 2007, 787–796.

Jeunieau, L., Alin, V. and Nagy, J. B., "Adsorption of thiacyanine dyes on silver halide nanoparticles: study of the adsorption site", *Langmuir* 16 (2), 2000, 597–606.

Jeunieau, L., Verbouwe, W., Rousseau, E., Auweraer, van der M., and Nagy, J.B., "Interaction of an oxa- and thiacarbocyanine dye and silver halide nanoparticles synthesized in a microemulsion system". *Langmuir* 16, 2000, 1602.

La Mer, V.K. and Dinegar, R.H., "Theory, production and mechanism of formation of monodispersed hydrosols". *J. Am. Chem. Soc.* 72, 1950, 4847.

Liao, J., Zhang, Y., Yu, W., Ge, C., Liu, J., Gu, N., Linear aggregation of gold nanoparticles in ethanol *Colloid. Surf.A* 223, 2003,177.

Liu, X. H., Luo, X. H., Lu, S. X., Zhang, J.C., and Cao, W. L., "A novel cetyltrimethyl ammonium silver bromide complex and silver bromide nanoparticles obtained by the surfactant counterion". *J. Colloid Interface Sci*. 307, 2007, 94–100.

Mafune F., Kohno, J., Takeda, Y. and Kondow, T. "Structure and stability of silver nanoparticles in aqueous solution produced by laser ablation". *J. Phys. Chem. B* 104, 2000, 8333.

Moroi, Y., Matuura, R. "Relationship between solubility and micellization of surfactants; micelle temperature range (MTR) instead of krafft point". *Bull. Chem. Soc. Jpn*. 61, 1988, 333.

Oleshko, V. P. "Size confinement effects on electronic and optical properties of silver halide nanocrystals as probed by Cryo-EFTEM and EELS". *Plasmonics* 3, 2008, 41–46.

Pal, S., Tak, Y. K. and Song, J. M., "Does antibacterial activity of silver 1 nano particle depend on shape of nano particle? A study on Gram-negative E. coli" *Appl. Environ. Microbio*. 73, 6, 2007, 1712.

Rao, C.N.R. A. Muller, K. Anthony Nanomaterials Chemistry: Recent Developments and New Directions, Wiley-VCH, (2007) 141-145.

Sambhy, V. MacBride, M., Peterson, B. R. and Sen, A., 'Silver bromide nanoparticle/polymer composites: dual action tunable antimicrobial materials". *J. Am. Chem. Soc.* 128 (30), 2006, 9798–9808.

Sturmer, D. M, Marchetti, A.P., Sturge, J., Waworth, V. and Shepp, A., *Imaging Processes and Materials* (Neblette's eighth ed.), Van Nostrand Reinhold, New York (1989) Chap. 3, p. 71.

Spirin, M. G., Brichkin, S. B. and Razumov, V. F., "Growth kinetics for AgI nanoparticles in AOT reverse micelles: effect of molecular length of hydrocarbon solvents". *J. Colloid Interface Sci*. 326, 2008, 117–120.

Tojo, C., Blanco, M. C., Rivadulla, F. and Lo´pez-Quintela, M. A. "Kinetics of the formation of particles in microemulsions" *Langmuir* 13, 1997, 1970-1977.

Tokay, B., Somer M., Ayse Erdem-S_enatalar, Ferdi S. C.and Thompson, R. W., "Nanoparticle silicalite-1 crystallization from clear solutions: Nucleation." *Microporous Mesoporous Mater*. 118, 2009, 143–151.

Tseng, K.-H., Huang, J. C., Liao C. Y., Tienb, D. C. and Tsung, T. T., "Preparation of gold ethanol colloid by the arc discharge method". *J. Alloy. Compd.* 472, 2009, 446–450.

Zhiyun, C. Fleet Erin, F. and Cooper G., "Applications of semiconductor nano-sized particles for photolithography". PATENT US007524616B2, 2009.

Chapter-4

Synthesis and characterization of silica nanoparticles in aqueous surfactant solutions

4.1 Introduction

Recently, many researches are going on to prepare and synthesis of silica nanoparticles, silica nanocomposite materials and mesoporous silica nanoparticles. The importance and advantages of nanometer-sized particles were shown not only in the scientific field, but also in various industrial applications, e.g. catalysts (Chen et al., 2009), pigments, pharmacy (Sun et al., 2005), etc. SiO_2 nanoparticles are used to make electronic substrates, thin film substrates, electrical insulators, thermal insulators, humidity sensors (Herbert et al., 1994), etc. The property of nanoparticles are highly depends on size of the particles. So it is necessary to develop good reliable commercial methods. There are various methods have been developed to control over particles size like aqueous methods, microemulsion, reverse microemulsion, sol-gel, thermal reaction, Chemical vapor deposition methods etc. But there are some difficulties like to control the size of particles, separation of particles from solution or control of size of particles.

In 1968, Stöber et al. reported a pioneering method for the synthesis of spherical and monodispersed silica nanoparticles from aqueous alcohol solutions of silicon alkoxides in the presence of ammonia as a catalyst, and different sizes of silica nanoparticles were prepared ranging from 50 nm to 2 µm with a narrow size distribution. After that many researcher have been studied silica nanoparticles to control of its size in various methods. These are microemulsion, reverse microemulsion, Sol-gel, aqueous solution, Chemical Vapors deposition, Thermal reaction, Surfactant system, spray precipitation methods etc. According to methods of preparation, the parameters change under different reaction condition. Different parameters have different effect on size of particles in same reaction system, according to which size of particle increases or decreases. Kota et al (2005) had studied the five parameter that affect particle size, as Bogush et al (1988) studied in alcohol medium, like effect of TEOS, effect of ammonia, effect

of alcohol, effect of water and reaction temperature by sol-gel methods. They have calculated R value according to concentration of TOES and water taken in the experiment.

In this paper we have focused on surfactant assistance alcohol-water system on the synthesis of silica nanoparticles. Silica nanoparticles in different surfactant medium have been synthesized. We have fixed the R value along with water concentration, then calculated concentration of TEOS and then we observed the change in particle size on varying the value of R. Along with different R value other parameters have been studied which finally controls the size of nanoparticles

Formation of silica nanoparticles are proceeds via two reactions: (i) Silanol groups are formed by hydrolysis reaction

$Si\text{-}(OC_2H_5)_4 + H_2O \longrightarrow Si\text{-}(OH)_4 + 4\ C_2H_5\text{-}OH$

(ii) Siloxane bridges are formed by a condensation polymerization reaction

$2\ Si\text{-}(OH)_4 \longrightarrow 2\ (Si\text{-}O\text{-}Si) + 4\ H_2O$

The two reactions, hydrolysis and condensation reaction depends on the various parameters that take part in the reaction. The size of particles can be controlled by varying the parameter. We have studied all these parameter to see the effect of final particle size.

4.2. Experimental

Materials

The reagents tetraethylorthosilicate (TEOS, 98%), cetyltrimethylammonium bromide (CTAB, 99%), Triton X-100 (TX-100, Laboratory grade, Cat no. 9002-93-1), sodiumdodecyl

benzenesulfonate (SDBS, technical grade, Cat no. 28 995–7) were obtained from Sigma-Aldrich, Germany. The reagent grade ethanol (99.9%), ammonium hydroxide (NH_4OH, 28 % aqueous solution), were purchased from Rankem, India, and used without purification. Ultra pure water of 18.2 MΩ.cm resistivity and pH 6.4 – 6.5 (Sartorius, Germany) was double distilled again and used for all the experiments. The silica particles were synthesized by modified Stöber methods. The molar concentration of precursor mixture TEOS: NH_4OH:C_2H_5OH was 0.003: 1: 1. The concentration of silica was varied from 0.1 to 50 mM. The water to TEOS ratios (R) was varied from 4 to 20. The concentration of surfactant was 3 × CMC of the individual surfactants. The reaction was carried out under sonication in regular time interval to prevent agglomeration.

4.3 Characterization

The particle size (diameter) and zeta potential were analyzed by dynamic light scattering (DLS) technique using a Malvern Zeta Size analyzer (Nano ZS, Malvern, U.K.). The samples were sonicated in a sonication bath for ~ 2 min just before the particle size analysis. The FT-IR analysis was done using Perkin- Elmer FT-IR spectrophotometer (S 2000, USA). The particle shape and size was observed under a SEM (JEOL, JSM-6480LV).

4.4. Results and Discussion

Different parameters have been studied to know the minimum size of silica nanoparticles in a fixed composition of the reactant. The silica nanoparticles were prepared by modified Stöber methods. The parameters such as concentration of TEOS, concentration of ethanol, concentration of ammonia solution, concentration of surfactant, effect of sonication, effect of R on a fixed composition, effect of time on particle size, have been studied.

4.4.1 Effect of TEOS

Stöber et al has reported that there is no effect of TEOS on final particle size. (Stöber et al., 1968) In contrast to that study, some researchers have also reported that particle size increases with the increasing concentration of TEOS (Bogush et al., 1988). In the present study we found both increasing and decreasing trend of particles size with the increasing concentration of TEOS. We varied the concentration of TEOS from 0.1 mM to 50 mM to see the effect of concentration at constant ratio of other reactant as mentioned above and the results are plotted in Figure 4.1. It has been found that the size of silica nanoparticles increases gradually with the increasing concentration of TEOS up to 5 mM, and then it decreases and again increases. The lowest size obtained was 266 nm at 0.1 mM concentration of TEOS and largest size was 625 nm at 5 mM TEOS concentration. The particles size obtained by DLS analysis also has good agreement with the size obtained from SEM as shown in Figure 4.2.

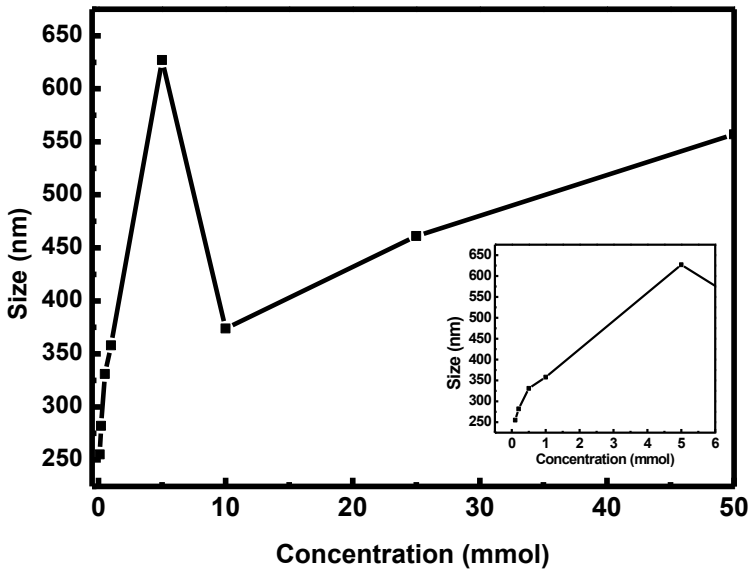


Figure 4.1 The effect of TEOS concentration on particle size of silica nanoparticles by DLS analysis.

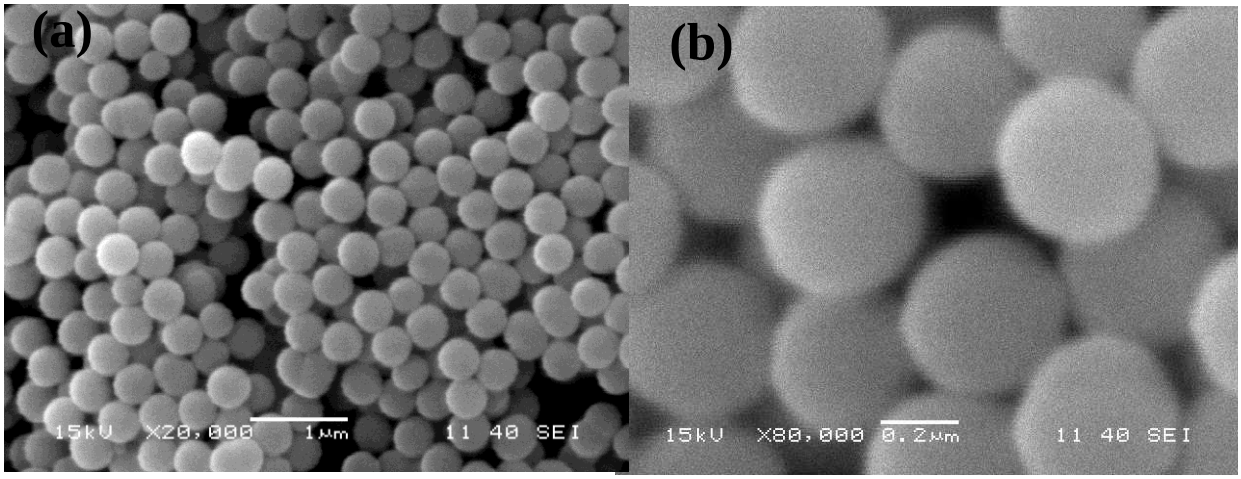


Figure 4.2 The SEM images of silica nanoparticles at 0.1 mM concentration

4.4.2 Effect of R

Since the particles were synthesized by sol-gel method, water also acts as reactant. So the effect of R (water to TEOS ratio) also affects the particle size. The *R* was varied from 4 to 20 in this study to see the change in particle size. We fixed the other reactant ratio and concentration of TEOS was 0.1 mM because we got lowest particle size in this concentration. The variation of *R* with particle size is shown in Figure 4.3. It can be seen that the lowest size of 250±8 was obtained at $R = 10$.

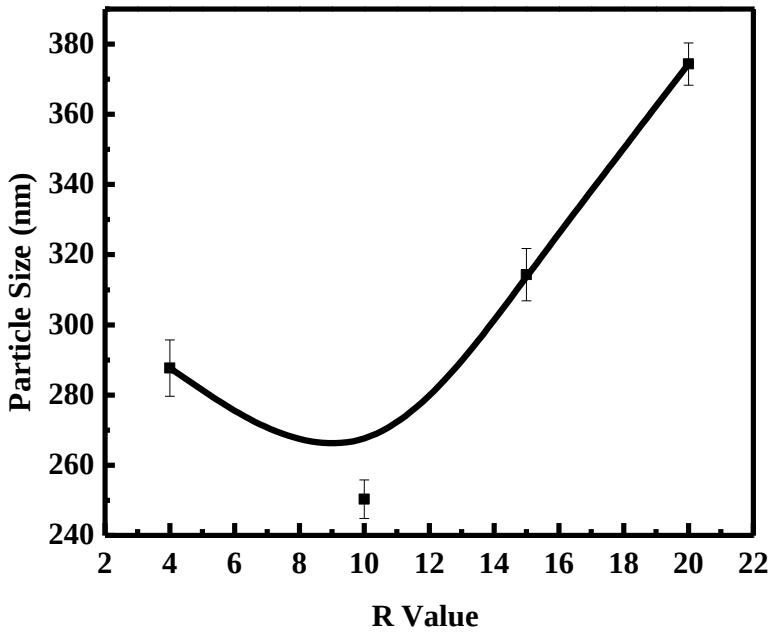


Figure- 4.3 The effect of R on particle size of silica nanoparticles.

4.4.3. Effect of Time

The reaction time is very important on the final particle formation. The minimum reaction time was determined in this section by FT-IR study. The FT-IR analysis was done after 5 min, 30 min and 1 day. The results are shown in Figures 4.4 and 4.5. It was found that the particles were formed within 30 minutes of reaction under stirring condition. From FTIR data it is clear that particles were formed within 30 minutes. Figure 4.4 shows FT-IR spectrum of pure TEOS and after 5 min of reaction. It can be seen that both the peaks merges without any difference, indicating 5 min is not sufficient to complete the reaction. However comparison with 30 min shows there is a distinct difference between the peaks. Further the spectrum of 30 min and 1 day are compared and found there is no difference (Figure 4.5), indicates reaction may completed within 30 minutes.

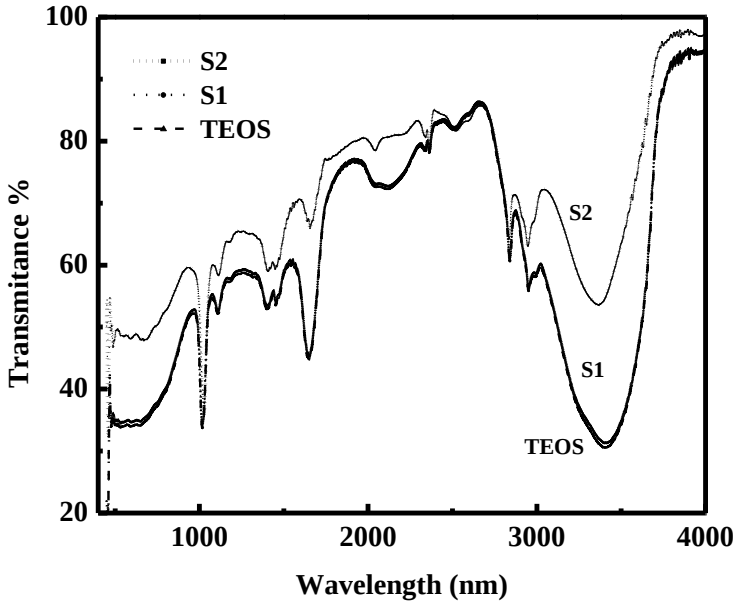


Figure 4.4 The FTIR spectra of TEOS, S1, the sample analyzed after 5 min, and S2, the sample analyzed after 30 min.

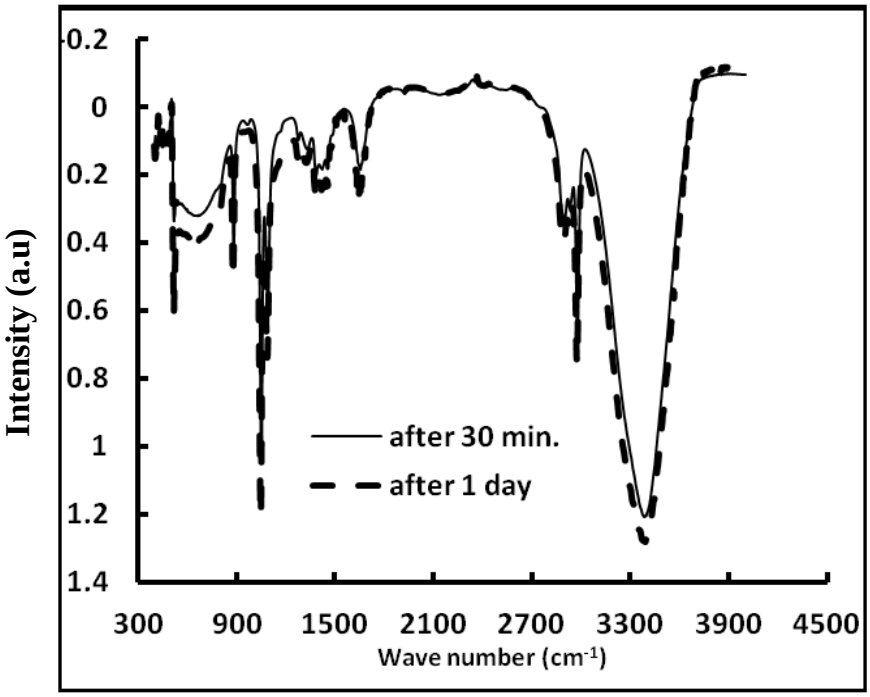


Figure 4.5 The FTIR spectra of silica nanoparticles at 0.1 mM concentration.

4.4.4. Effect of sonication

The effects of sonication play an important role on particle size synthesized in aqueous media. The sonocation effect was studied on different reactant concentration and found lower particle size for the system under sonication. In this study two reaction mixtures were prepared simultaneously one was kept in a sonication bath during the reaction for 3 min and another without any disturbance. The particle sizes for different concentrations are presented in Table 4.1. It can be seen from the table that the particle size obtained under sonication is almost half to that of without sonication.

Table-4.1 The effect of sonication on particle size of silica.

Concentration of TEOS (mM)	Particle size (nm)	
	Without sonication	Sonication
0.1	433	259
0.5	572	282
1	713	358
5	927	627
10	745	373

4.4.5. Effect of ammonium hydroxide (NH_4OH)

The ammonium hydroxide acts as catalyst. It controls the pH, which is very important for reaction condition. Many authors have been reported SiO_2 can be prepared in both acidic and alkaline medium. So the pH should more or less, not neutral. In neutral condensations may not occur. As we know formations of silica undergo three basic steps as hydrolysis, alcohol condensation and water condensation. If condensation does not occur the silica will not form.

We found that pH 11 is very good condition for the reaction. If pH lowers than 11 the reaction was slow. The small (necessary) amount of ammonium hydroxide only required for carried out the reaction. The ammonium hydroxide acts as catalyst mean it will not consumed in the product formation. At constant concentration of precursor solution, the number of reactant is fixed. If more amount of ammonium hydroxide is added, it would react with same number of reactant, not more. So adding more amount of ammonium hydroxide has no effect on particles formation.

4.4.6. Effect of alcohol (EtOH)

Alcohol is very essential component for formation of Silica particles. It gives basis for condensation reaction. The condensations reactions are responsible for gel formation (Cellesi et al., 2006). The proper ratio of alcohol is required to prevent from gel formation. We observed TEOS to C_2H_5OH ratio (0.003:1) was good for particle formation by modified Stöber methods. Otherwise it leads to gel formation. On decreasing the alcohol amount at constant reaction condition, gel was frequently formed (Table-4.2). Even on absent of alcohol, reaction took place. We got the small glass like transparent films due to lack of condensation.

Table-4.2 The gel formation due to change in alcohol amount.

TEOS: C_2H_5OH	Gel like appearance
0.003:1.5	No
0.003:1	No
0.003:0.6	No
0.003:0.4	Yes
0.003:0.1	Yes

4.4.7 Effect of Surfactant

The surfactant is commonly used for surface modification of different nanoparticles. Here we have studied three different surfactant like nonionic surfactant (TX-100), anionic surfactant (SDBS) and cationic surfactant (CTAB). To study the surfactant effect we used four different concentrations of precursor solutions (0.1 mM, 0.5 mM, 1mM, and 5 mM) and three CMC of the surfactant solution. The particle size at lower concentration was almost same. On increasing the concentration of precursors, the different trends were observed. The surfactant has minimum effect at lower concentration of precursor's solution. On comparison with aqueous solution (without surfactant), the particles formed in presence of CTAB has shown similar trend as in aqueous solution, but bigger size than the aqueous solution. The particles were formed in presence of TX-100 are much smaller compare to others in a wide range of reactant concentration. But the smallest particles were formed in presence of SDBS at 0.1 mM of precursor solution. Since the silica particles are negatively charged in aqueous media cationic surfactant CTAB adsorbed thorough the head group of the surfactant molecule and make the surface hydrophobic. As a result, may be because of van-der Waals attractive force between the particles agglomeration tendency is more which in turn gives larger sized particles.

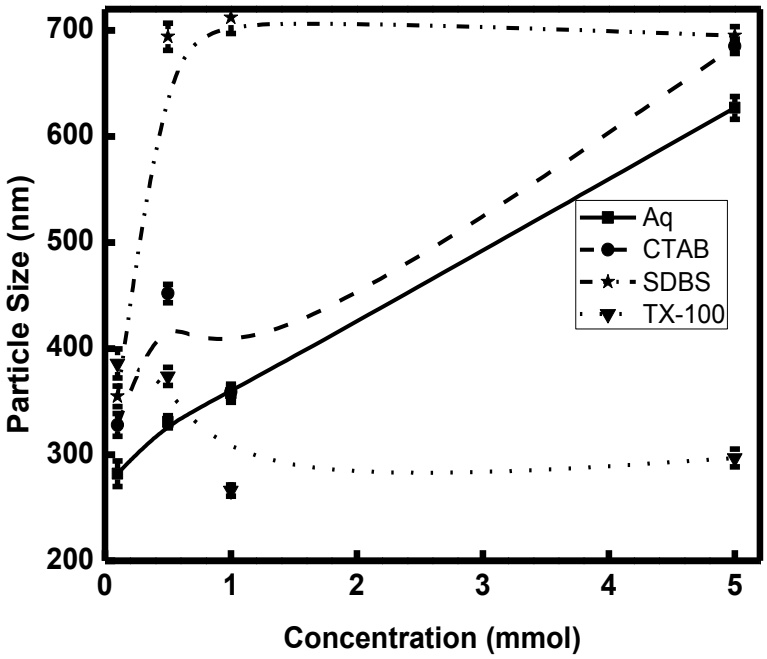


Figure 4.6: The particle size of silica nanoparticles in the presence of surfactant solutions obtained by DLS measurements.

The minimum and maximum sized particles obtained in the presence of CTAB are 328±8 and 740±7 nm respectively. In case of SDBS the mechanism is not very clear. As the surfactant and particles both are negatively charged probably surfactants are not adsorbing on the particle surface. In this situation probably inter particle interaction is more than that of particle-surfactant interaction. In case of TX-100, initially there is an increasing trend of particle size at lower concentration of TEOS; finally the size is constant over a wide range of concentration. On the surface of silica nanoparticles some surfactant molecules may be adsorbed through the polyethylene oxide head group via hydrogen bonding and some may be through their tail group. Finally, after the adsorption because of the hydration of the surfactant molecules and steric repulsion prevents agglomeration, as a result gives a uniform particle size over a wide range of

concentration. The particles obtained in the presence of different surfactants are presented in Figure 4.7.

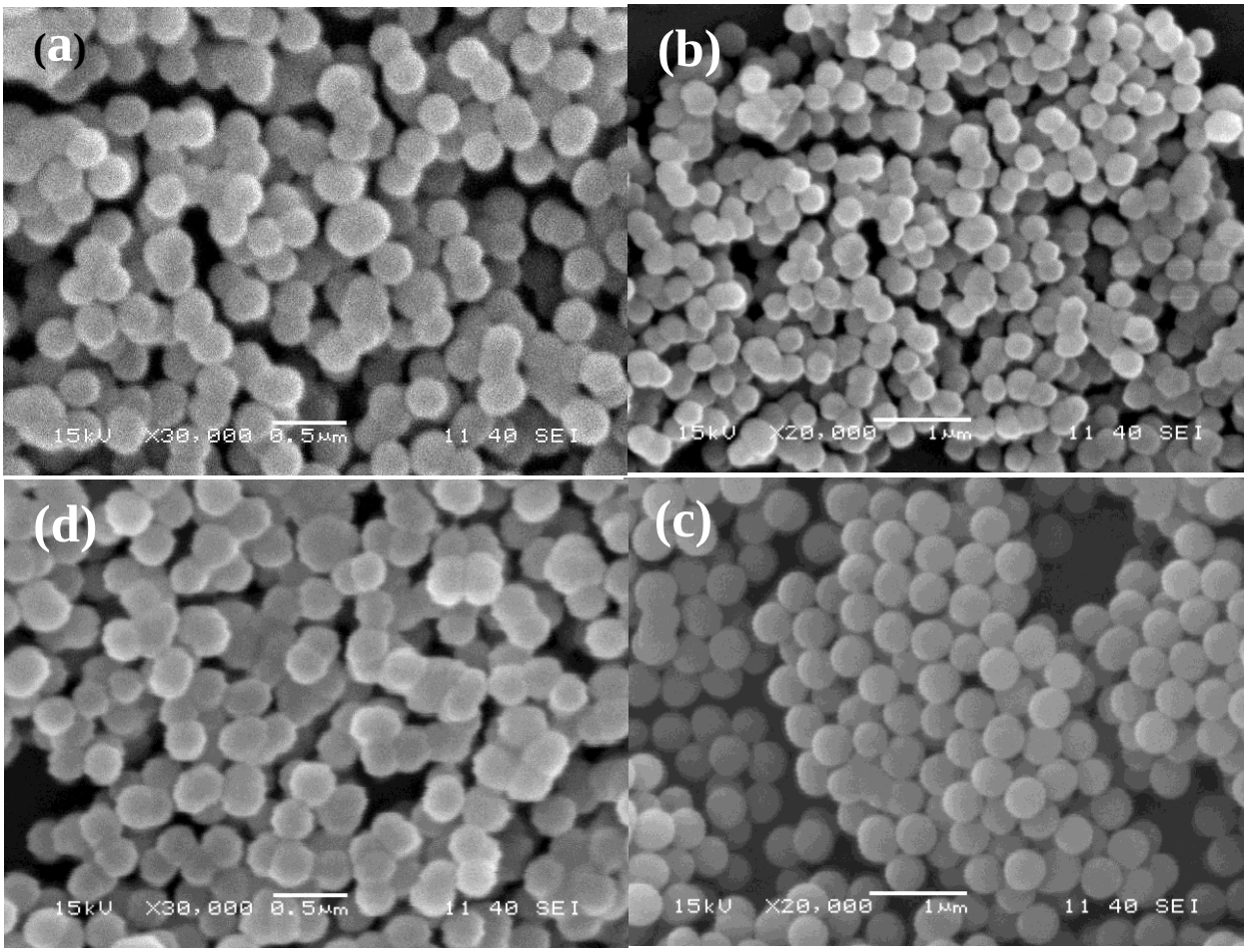


Figure 4.7: The SEM images of silica nanoparticles in CTAB (a), TX-100 (b), aqueous solution (c), and SDBS solution (d) from 0.1 mM TEOS concentration.

4.5. Conclusion

The silica nano and micro sphere were successfully prepared by modified Stöber methods. The growth of particles was studied in different surfactant solution. The interesting result of particles size was given by TX-100 solution. Even high concentration (5 mM) of precursor's solution, it did not allow to grow big particles. So we got smaller size of particle compared to other

surfactant. We found that every parameter has effect on particle size. The concentration of precursor has effect on particle size, but there is no regular manner. The particle size increase linearly up to certain concentration, then it follows both decreased and increased trend. Along with time the particle growth takes place. It is expected that particle growth finished within 30 minutes of reaction started, shown by FTIR and DLS data. The sonication has a good impact on particle size; it opposes the agglomeration among the particles. The particle size is reduced to half under sonication. Similarly alcohol provides easy of reaction and control of size. The proper amount of reaction prevents from gel formation.

REFERENCES

Bogush, G.H. Tracy, M. A. Zukoski, C.F., "Preparation of monodisperse silica particles: Control of size and mass fraction". J. Non-Cryst. Solids 104 (1988) 95

Chen C., Ying Li, Liu S. "Fabrication of macroporous platinum using monodisperse silica nanoparticles template and its application in methanol catalytic oxidation". J. Electroanalytical Chem. 632 (2009) 14

Herbert G. "Medical and Technological Application of Monodispersed Colloidal Silica Particles". J. Eur. Ceram. Soc. 14 (1994) 205.

Kota S. Rao , El-Hami K., Kodaki T., Matsushige K., MakinoA, K., 'Novel method for synthesis of silica nanoparticles" J. Colloid Interface Sci. 289 (2005) 125.

Stöber W., Fink A., Bohn, E., "Controlled growth of monodisperse silica sphere in the micron size ranges". J. Colloid Interface Sci. 26 (1968) 62.

Sun Bingyun, Mutch Sarah A., Lorenz R. M., and Chiu Daniel T. "Layered Polyelectrolyte-Silica Coating for Nanocapsules". Langmuir, 21, 2005, 10763.

Chapter-5

Synthesis and characterization of $AgBr/SiO_2$ core/shell nanoparticles in aqueous surfactant solutions

5.1. Introduction

Core/shell nanoparticles have attracted more attention over the simple nanoparticles because of their wide ranges of applications. Till now many researchers have developed core/shell structure of many new nanomaterials. The properties of core/shell nanomaterials are directly related with particle size and shape, (Lieber et al 1998) inter-particle distance and characteristics of protective shell. For example Au acts as catalyst in nano-ranges.and depending on its size, its shows different color (Shimizu et al 2003). The shell materials also affect the materials property. The silica coating on gold nanoparticles makes it biocompatible (Kumar et al. 2006). The core-shell nanoparticles are nanostructure that have core made of a material coated with another material. The necessity to sift to core-shell structure that the improvement of the properties of the materials. The shell materials are chosen according to specify property of the materials and it also prevent agglomeration of the core particles.

There are many studies on silica and its coating has been done. Silica particles have been used as shell material due to its colloidal stability. Zhang et al has been prepared gold-silica core-shell materials by sol-gel methods. They have been investigated the structure and stability of the core-shell materials with the induction of temperatures. They have been found that in the interface Au-Si bond is stable up to 600-1000 °C. Similarly Badr et al (2007) also coated silica on the different metal core like silver, gold nanoparticles and studied photo degradation of methyl orange dye. They used SiO_2 as a photo catalyst for degradation of methyl orange dye. The polystyrene, Iron Oxide (Xu et al. 2006) core, TiO_2 core (Park et al 2005), are coated with silica shell by reverse emulsion methods. From literature we found that silica is coated by three methods, sol-gel method, emulsion methods and modified Stöber methods. Among these methods reverse emulsion is used for formation of very small particles, but separation is difficult.

The modified Stöber method is very easy and robust method to form silica layer on the core materials. The core material surfaces are modified by different reagents to make suitable for coating of silica layers. The different surfactant has been mainly used for surface modification for example hexadecyltrim-ethyl ammonium bromide (HTAB) (Kim et al 2009), cetyltrimethylammonium bromide (CTAB) (Pastoriza-Santos et al 2006, Wang et al 2011, Guo et al 2009), benzethonium chloride (BTC) (Du et al 2009).

In this study we have chosen AgBr as core material and CTAB surfactant as capping agent as well as surface modifier. The positive surface charge over the core surface will favor coating of negatively charged silica on it to get a core/shell structure.

5.2. Experimental

5.2.1. Materials

Tetraethylorthosilicate (TEOS, 98%), cetyltrimethylammonium bromide (CTAB, 99%) was obtained from Sigma-Aldrich, Germany. The reagent grade silver nitrate ($AgNO_3$, 99.9%), potassium bromide (99.3%) Ethanol (99.9%), ammonium hydroxide (NH_4OH), were purchased from Rankem, India, and used without purification. Ultra pure water of 18.2 MΩ.cm resistivity and pH 6.4 – 6.5 (Sartorius, Germany) was double distilled again and used for all the experiments.

5.2.2. Synthesis of Silver Bromide nanoparticles

The silver bromide nanoparticles were prepared by simple precipitation reaction of silver nitrate with potassium bromide. $AgNO_3$ solution was added to potassium bromide solution under mixing condition in a cyclomixer to get AgBr nanoparticles in the aqueous solution. Fresh silver nitrate solution was prepared and used for each experiment to avoid photo oxidation of the $AgNO_3$ solution. The constant temperature of the solution was maintained throughout the

experiment using a water bath circulator. The different concentration of precursor solution was used under same condition.

5.2.3. Synthesis of Silica Particles

The silica particles were synthesized by Stöber methods. The molar concentration of precursor mixture TEOS: NH_4OH: C_2H_5OH were 0.003: 1: 1. The concentration of silica was varied from 0.1 mM to 50 mM. The silica particles also formed in CTAB, TX-100 surfactant solution to observe the change in particle size. The reaction was carried out under sonication in regular time interval.

5.2.4 Synthesis of silver bromide-silica core-shell nanoparticles.

The $AgBr/SiO_2$ core-shell had been prepared by modified Stöber methods. The AgBr nanoparticle was prepared in aqueous solution and then equimolar concentration of CTAB was mixed to it under cyclomixer. In a single reaction vessels all the reactant were mixed under continuous stirring condition for 1 hour and then the particles were separated by centrifugation and followed by ethanol wash.

5.3. Characterization

The sample was sonicated in a sonication bath for ~ 2 min just before the particle size analysis. The particle size (diameter) and zeta potential were analyzed by dynamic light scattering (DLS) technique using a Malvern Zeta Size analyzer (Nano ZS, Malvern, U.K.). The UV absorption was studied spectrophotometrically using a UV-Vis-NIR spectrometer (UV-3600, Shimahdzu, Japan). The fluorescence spectra were measured using fluorescence spectrophotometer (Hitachi

F-7000, Japan). The particle shape and size was observed under a SEM (JEOL, JSM-6480LV). TEM samples were prepared after drying on carbon coated copper grid and observed under a transmission electron microscope (FEI, Model: STWIN) with an accelerating potential of 200 KV and the images were analyzed with TECNAI G 2 software.

5.4. Results and discussion

Silver bromide nanoparticles were synthesized in aqueous solution in the presence of CTAB, where the counter ion was used as source of bromide ion. After the mixing of the reactants, particles formation was initially supported by UV-Vis spectrophotometer. The UV-Vis absorption spectra of the reaction solution showed absorption maxima at 236 nm (Figure-5.1) and with time the intensity of the peak decreases up to certain level, and then becomes constant. This is because of the growth of the particles, and finally reaches to an equilibrium size. The surface of the AgBr nanoparticles was modified using CTAB surfactant. The adsorption of CTAB on AgBr surface was confirmed by zeta potential measurement. The zeta potential of the pure AgBr was -19 mV, but adsorption of CTAB the surface charge was positive (+47 mV). So the shell materials of opposite charge can be easily coated on it. The particle diameter of AgBr measured by DLS was 80±4 nm synthesized from 0.1 mM concentration of reactant solution. It has been shown before that the particle size of AgBr is highly dependent on reaction concentration, with the increasing reactant concentration, particles size decreases. However the surface charge does not change on changing the concentration of reactant solution. The surface charge of the particles depends on concentration of the surfactant used. The zeta-potential gradually increased with increasing concentration of surfactant (upto 0.05 mM). The zeta-potential reaches to a constant value near the CMC of CTAB.

The silica nanoparticles were synthesized in modified Stöber method. The particles size of silica nanoparticle was 250±10 nm in CTAB solution. The particles were characterized by FTIR, SEM, and EDX after formation. The size of the particles mainly depends on the concentration of TEOS under the same experimental condition. The concentration of ammonium hydroxide and ethanol has also effect the final particle size. We standardized and fixed the concentration of ethanol and ammonium hydroxide, where may get lower size of the silica nanoparticles.

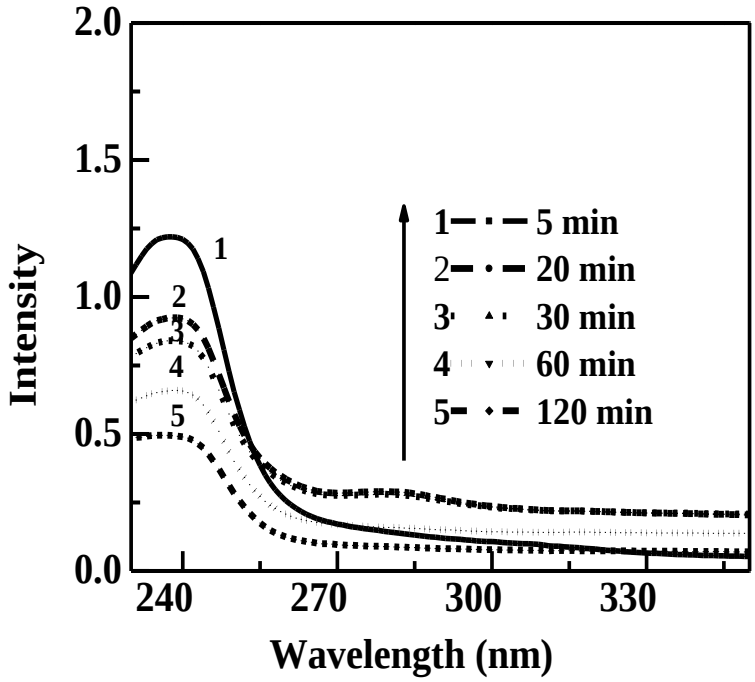


Figure-5.1 The absorption spectra of AgBr in CTAB solution of 0.1 mM concentration of $AgNO_3$

5.4.1. Silica coated AgBr nanoparticles

Silica was coated on AgBr nanoparticles by modified Stöber method after the formation of AgBr core in-situ. The lowest particle size of 90±8 nm $AgBr/SiO_2$ core/shell nanoparticles was obtained in this method. It is found that on varying the concentration of TEOS, the size of

core/shell nanoparticles increases. The core/shell particle size varied from 95 to 430 nm by changing TEOS concentration. The bigger size particles were found at higher concentration of TEOS because of increasing shell thickness. The shell thickness was varied from 5-340 nm. Figure 5.3 shows the effect of TEOS concentration on overall size of core/shell nanoparticles. The concentration of CTAB is also important to get proper coated nanoparticles; a minimum 0.05 mM CTAB concentration is required to get coated particles.

The silica was coated on AgBr nanoparticles and conformed from SEM and TEM images (figure-5.5). At 0.1 mM of CTAB AgBr nanoparticles were isolated in silica shell, indicates CTAB concentration were optimal for the formation of monolayered structures on AgBr surfaces. The shell thickness was very thin 5 nm. The samples were excited at 270 nm wavelength and measured the emission spectra. The emission spectra of AgBr nanoparticles found at 542 nm and high intensity. But on coating with silica, the intensity of the spectra decreased (figure-5.3). We have compared the two figure, one is silica coated AgBr ($AgBr/SiO_2$) and other is mixture of both core-AgBr and silica ($AgBr + SiO_2$) nanoparticles. It is clearly shown that the intensity is different for both due to coating of silica, the intensity decreased in case of AgBr/silica core-shell materials. But in case of mixture, silica and AgBr formed separately, so AgBr gives more intense peak as free AgBr at 542 nm with full width at half-maximum (FWHM) is 4.8 nm, where as the $AgBr/SiO_2$ gives full width at half-maximum (FWHM) .is 4.2 nm.

The silica is coated on AgBr due to electrostatic attraction between the particle and shell materials. The core AgBr surface was modified using CTAB surfactant. The zetapotential of AgBr changes from -19 mV to +45 mV. The zeta potential gives stability to the particles due to electrostatic repulsion between the particles –particles. The zetapotential of silica on constant

ratio of ammonium hydroxide and ethanol was -15 mV. The core particle and shell are of opposite charges, so the electrostatic attraction is the driving force to coat the silica particles.

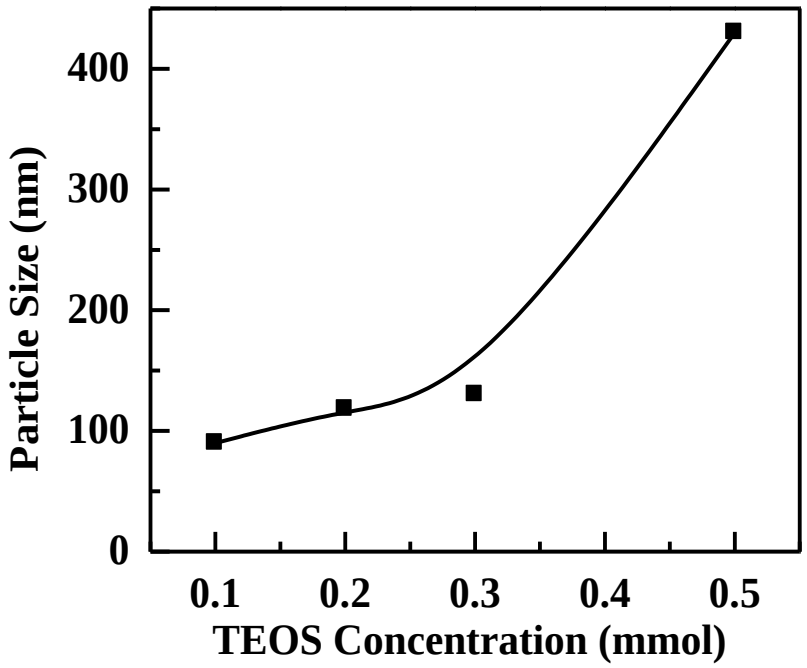


Figure-5.2 The particle Size of $AgBr/SiO_2$ core-shell with concentration of TEOS

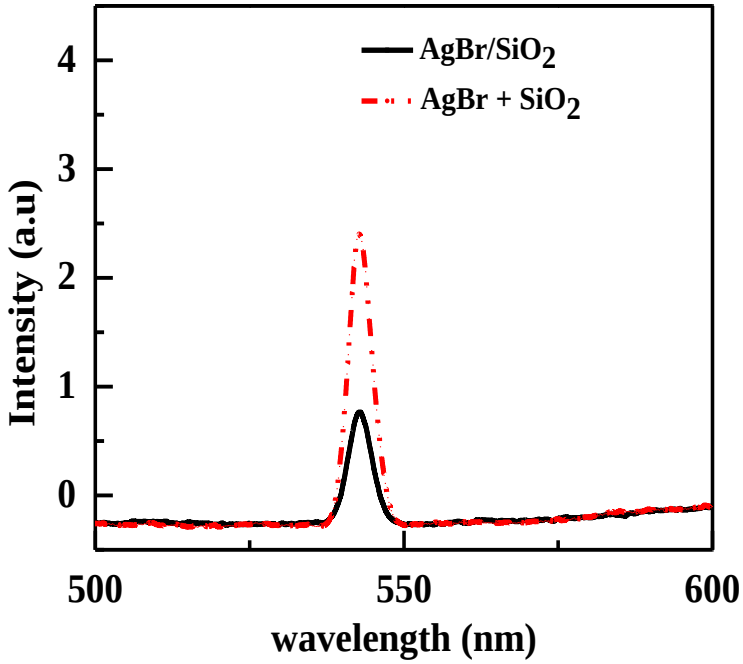


Figure-5.3 Fluorescence spectra of core/shell particles ($AgBr/SiO_2$) and separately added individual mixture of AgBr nanoparticles and Silica. ($AgBr+SiO_2$)

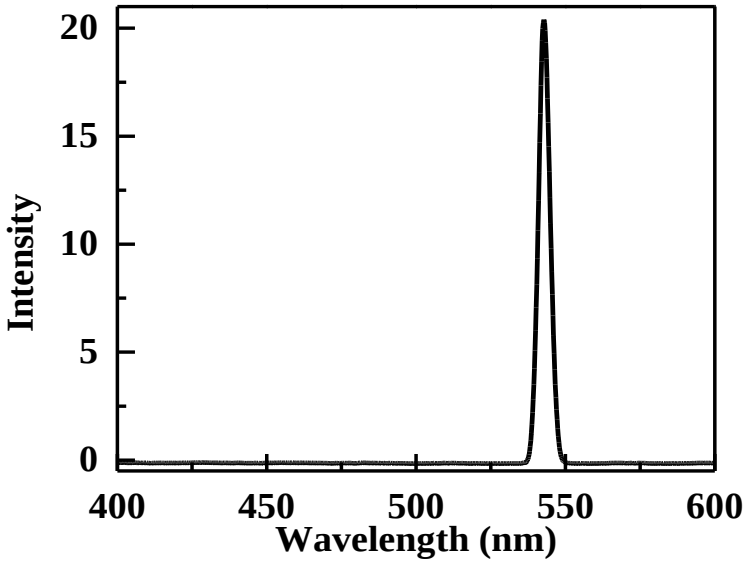


Figure-5.4 Fluorescence spectra of pure AgBr nanoparticles

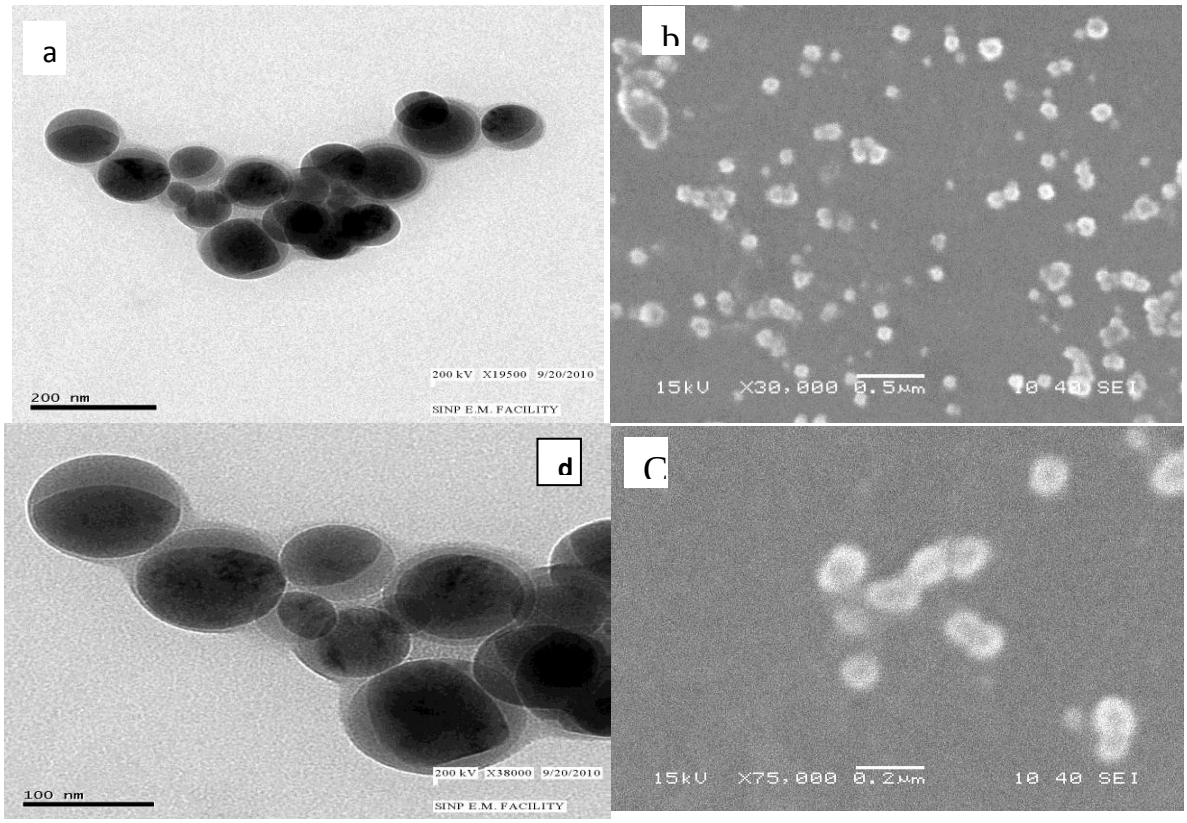


Figure-5.5 TEM and SEM images of Core/shell particles

5.5. Conclusion

The surface properties of silver bromide nanoparticle are successfully modified using surfactant solution. The $AgBr/SiO_2$ core-shell nanoparticles have been prepared within 100 nm by modified Stöber methods. The spherical composite materials are formed. The shell thickness can be controlled on varying the concentration of precursor's solution. Silica can be coated on other material by modifying the surface of the core shell materials.

REFERENCES

Badr Y., Mahmoud, M. A., 'Photocatalytic degradation of methyl orange by gold silver nano-core/silica nano-shell' J. Phys.Chem Solids 68, 2007, 413–419

Du, H., Hamilton, P. D., Reilly, M. A., Avignon, A., Biswas, P., 'A facile synthesis of highly water-soluble, core–shell organo-silica nanoparticles with controllable size via sol–gel process'. J. Colloid Interf. Sci. 340, 2009, 202–208

Gou, X., Liu, X., Xu, B., Dou, T., 'Synthesis and characterization of carbon sphere-silica core–shell structure and hollow silica spheres' Colloids Surf. A: Physicochem. Eng. Aspects 345, 2009, 141–146

Kim, S. G., Hagura, N., Iskandar, F., Okuyama, K. 'Characterization of silica-coated Ag nanoparticles synthesized using a water-soluble nanoparticle micelle'. Adv. Powder Tech 20, 2009, 94–100

Kumar A, Pushparaj VL, Murugesan S, Synthesis Of silica-gold nanocomposites and their porous nanoparticles by an in-situ Approach. Langmuir, 22, 2006, 8631-8634.

Lieber Charles M., 'One-dimensional Nanostructures: Chemistry, physics and application'. Solid State Comm. 107, 1998, 607-616.

Shimizu, T., Teranishi, T., Hasegawa, S., Miyake, M., 'Size Evolution of Alkanethiol-Protected Gold Nanoparticles by Heat Treatment in the Solid State' J. Phys Chem B 107, 2003, 2719

Park O. K., Kang Y. S. 'Preparation and characterization of silica-coated TiO_2 nanoparticles.' Colloids Surf. A: Physicochem. Eng. Asp 257, 2005, 261–265

Pastoriza-Santos, I.; Pe´rez-Juste, J.; Liz-Marza´n, L. 'Silica-Coating and Hydrophobation of CTAB-Stabilized Gold Nanorods' Chem.Mater. 18, 2006, 2465.

Wang, S., Zhang, M., Wang, D., Zhang W., Liu, S., 'Synthesis of hollow mesoporous silica microspheres through surface sol–gel process'.on polystyrene-co-poly(4- vinylpyridine) core–shell microspheres'. Micropor. Mesopor. Mater 139, 2011, 1–7.

Xu, H., Cui L., Tong, N., Gu. H. 'Development of high magnetization Fe_3O_4 / polystyrene / Silica nanospheres via combined miniemulsion / emulsion polymerization'. J. Am. chem. Soc. 128, 2006, 15582

Chapter-6

Conclusion

6.1. Conclusion

In the study, AgBr/SiO_2 core/shell nanoparticles were prepared in aqueous chemical method. Before synthesizing core/shell nanoparticles, core (AgBr) and shell (SiO_2) particles were synthesized separately and different parameters on particle size were also studied. Spherical AgBr nanoparticles were prepared in aqueous media in the absence and presence of surfactant. Smaller particles were obtained in pure aqueous media by increasing the reactant concentration. The coarsening rate constant for the particle formation was found to increase linearly with increasing reactant concentration. The presence of nonionic surfactant generated smaller particles than were obtained in pure aqueous media. The coarsening rate constant in the presence of TX-100 was always lower than that in the presence of pure aqueous media. In pure aqueous media, the temperature effect caused an increase in particle size as the temperature was increased from 20 to 30 °C, after which the change was not significant. In contrast, in the presence of TX-100, the change was not significant in the 20 - 30 °C temperature ranges, but a further increase to 40 °C resulted in a significant change in size.

Similarly the individual shell material (Silica nanoparticle) has been prepared by modified stöber method and different parameter had studied. The interesting result of particles size was given by TX-100 solution. Even high concentration (5 mM) of precursor's solution, it did not allow to grow big particles. So we got smaller size of particle compared to other surfactant. We found that every parameter has effect on particle size. The concentration of precursor has effect on particle size, but there is no regular manner. The particle size increase linearly upto certain concentration, then it follows both decreased and increased trend. Along with time the particle growth takes place. It is expected that particle growth finished within 30 minutes of reaction started, shown by FTIR and DLS data. The sonication has a good impact on particle size; it opposes the

agglomeration among the particles and controls the nucleation also. The particle size is reduced to half under sonication. Similarly alcohol provides easy of reaction and control of size. The proper amount of reaction prevents from gel formation.

Finally on combination of two nanoparticles, we prepared core/shell nano structures. Here silica is coated over silver bromide nanoparticles by modified Stöber methods. The surface properties of silver bromide nanoparticle are successfully modified using surfactant solution. The $AgBr/SiO_2$ core-shell nanoparticles have been prepared within 100 nm by modified Stöber methods. The spherical composite materials are formed. The shell thickness can be controlled on varying the concentration of precursor's solution.

6.2. Suggestion for future work

- Synthesis of hollow silica nanoparticles: AgBr core can be removed by NH_4OH treatment to get silica hollow nanoparticles.
- Other hollow nanoparticles can be synthesized using same AgBr template as core.
- Surface area and other surface property can be studied using the hollow nanoparticles.

Research Publication

Journal Published

Minaketan Ray, Santanu Paria, 'Growth kinetics of silver bromide nanoparticles in aqueous surfactant solutions'.***J. Ind. Eng. Chem. Res.,*** 2011, 50 (20), 11601–11607.

Conference

Preparation of Silver Bromide Nanoparticles in Aqueous TX-100 and CTAB Solutions, Minaketan Ray and Santanu Paria, p 23, 2009 CHEMFERENCE ' 09, IIT Madras.